



# Synthesis and Characterization of Fe<sup>II</sup>, Co<sup>II</sup>, Ni<sup>II</sup>, Cu<sup>II</sup> and Zn<sup>II</sup> Complexes With Dithiocarbamate and N-Donor Ligands

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## Abstract

New complexes of first series of transition metals with P-amino benzene dithiocarbamate of the general formula  $[M(PABdte)_2]$  and  $[M(PABdte)_2(L)_n]$  M=Fe( II ),Co( II ),Ni( II ),Cu(II) and Zn (II).

PABdte = Paraamino benzene dithiocarbamate ,n=2 when L= Py, $\gamma$ -Pic,iso quonoline ,3,5-lutidine

n=1when L=1,10-phenanthroline, en, 2,2bipy.and the type(R)<sub>4</sub>N[Ni(PABdte)<sub>3</sub>]

R= methyl, ethyl are prepared.

Physico chemical characterization of these complexes was applied using magnetic susceptibility measurements, molar conductance , Infrared and electronic spectra,

Metal content measurements, molar conductance indicate complexes of the type  $[M(PABdte)_2]$  and  $[M(PABdte)_2(L)_n]$  are non-electrolyte while complexes of the type (R)<sub>4</sub>N[Ni(PABdte)<sub>3</sub>] are 1:1 electrolyte. Magnetic moment and electronic spectra indicate that the complexes of the type  $[M(PABdte)_2]$  are tetrahedral geometry while the complexes of the type  $[M(PABdte)_2(L)_n]$  and (R)<sub>4</sub>N[Ni(PABdte)<sub>3</sub>] have octahedral geometry.

**Key words:** Dithiocarbamate , complexes, transition metal

## Introduction

Metal complexes play an essential role in agriculture, pharmacy, medicine and chemical industries[1]. Complexes of salicylaldehyde were among the first systems which were studied by infrared spectroscopy[2]. Similarly dithiocarbamate metal complexes are known for their dithiocarbamate metal complexes which are known for their various applications[3] which include vulcanization accelerators, high pressure lubricants, and active ingredients of fungicides, pesticides and pharmaceutical products.[4,5,6]

This kind of compounds has been reported in literature to show detoxicant and immunopharmacological properties such as antibacterial, antifungal etc[7], also they have been reported as a group of useful bridging ligands for creating mixed valence polynuclear systems[8]. An extensive search through literature showed that many mixed ligand dithiocarbamate complexes with Schiff base moiety as a part of its coordination ligand have been widely reported[8].

In this work we report on the synthesis and characterization of Fe(II), Co(II), Ni(II), Cu(II), and Zn(II) complexes with dithiocarbamate ligand 4-aminobenzene dithiocarbamate and N-donor ligands.

## Experimental

All reagents and solvents were of analytical grade and used as supplied from Fluka or BDH chemical companies. Infrared spectra which were recorded on Bruker Tensor 27 FTIR spectrophotometer in 400-4000  $\text{cm}^{-1}$  range using KBr discs and CsI discs in the range 4000-2000

Conductivity measurements were carried out on  $10^{-3}\text{M}$  solution of the complexes in DMF using conductivity meter PCM3 Jenway at ambient temperature. The electronic spectra were recorded on Shimadzu UV-visible spectrophotometer UV-160 for  $10^{-3}\text{M}$  solution of complexes in DMF as a solvent at  $25^\circ\text{C}$  using 1cm quartz cell. Metal content was determined using AA670 atomic absorption. Melting point was recorded on an electrochemical 9300 apparatus and uncorrected. The magnetic measurements were carried out on the solids by Faraday's method using Bruker BM6 instrument.

### 1.1 Preparation of sodium p-phenylene diamine dithiocarbamate :

The p-phenylene diamine dithiocarbamate ligand (PABdtc) was prepared by literature method [7] by adding (0.1mol, 10.81g) of p-phenylene diamine dissolved in  $15\text{ cm}^3$  distilled water to a solution (0.1mol, 4.0g) of sodium hydroxide with reflux 30 minutes and continuous stirring. The resulting mixture was cooled in ice and (0.1 mol, 76g) carbon disulfide was added dropwise with continuous stirring. The crude product was extracted by ether, the form precipitate was filtered off, washed with ether and dried. The reaction is shown in figure(1).

### 2.1 Preparation of complexes $[\text{M}(\text{PABdtc})_2]$

M= Fe(II), Co(II), Ni(II), Cu(II), Zn(II)

To a solution containing (0.001 mol) of the required salt  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ,  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ ,  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  in a small amount of water/acetone 20/80 respectively was added to (0.002mol) of sodium PABdtc. The mixture was stirred for about 30 minutes, then the precipitate was filtered, washed several times with acetone and finally air dried, other complexes were prepared by the same procedure. The reaction is shown in figure (2).

## 2.2 Preparation of complexes $[M(\text{PABdtc})_2(\text{L})_2]$

L= Py,  $\gamma$ -Pic, 3,5-lutidine, Isoquinoline

In to a solution containing (0.002mol,0.412g) of Na-PABdtc ligand dissolved in 10cm<sup>3</sup> acetone/ water 80/20 was added to (0.001mol)of metal salt and (0.002 mol,0.158g) of pyridine was added .The mixture was continuously stirred for 30 mint .The precipitate formed was filtered and washed with acetone and dried. other complexes of nitrogenous base prepared by the same procedure above. The reaction is shown in figure (3).

## 2.3 Preparation of complexes $[M(\text{PABdtc})_2\text{L}]$

M= Fe ( II ),Co( II ), Ni( II ), Cu ( II ), and Zn( II )

L= en , 1,10 -phen, 2,2-bipy.

The complexes prepared by the same procedure were shown in 2-1 and add (0.001mol,0.1982g) of 1,10-phen. dropwise with continuous stirring for 30 mint. The precipitate formed was filtered and washed with acetone and dried. The reaction is shown in figure (4).

## 2.4 Preparation of complexes $(\text{R})_4\text{N}[\text{Ni}(\text{PABdtc})_3]$

R= methyl, ethyl.

To a solution of (0.003mol) of Na- PABdtc dissolved in ethanol was added (0.001mol)of tetramethyl ammonium chloride dissolved in distilled water was added The mixture was stirring (0.001mol of  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ) The precipitate was filtered off and washed with acetone and dried. The reaction is shown in figure (5).

## Results and discussion

The new ligand was prepared for the reaction of P-phenylenediamine with sodium hydroxide then reflux 30 mint then added carbon disulfide, the complexes were prepared through direct reaction of the metal salt,  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  or  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  or  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  or  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  or  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  hydrous with the above ligand in (1:2) molar ratio. The values of conductivity in dimethyl formamide solution of the complexes range from (1.7-16.77) $\Omega^{-1} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$  which are typical values for non electrolyte type [9] while complexes of the type  $(\text{R})_4\text{N}[\text{Ni}(\text{PABdtc})_3]$  are 1:1 electrolyte.

## Infra-red spectral studies

The important IR band of ligand and its complexes are listed in table( 2). The stretching frequency of the  $\nu$  (C=N) band for the dithiocarbamates was intermediate between the stretching frequencies associated with typical single and double bonded carbon and nitrogen atoms [10]. The  $\nu$  (C=N) and  $\nu$  (C=S) were observed in the ranges of (1500-1550)  $\text{cm}^{-1}$  and (900-980) $\text{cm}^{-1}$  . The presence of only one band in the later region reports the bidentate

coordination of the dithio ligand [11]. The (N-H) band of dithiocarbamate was observed in the range (3319-3455  $\text{cm}^{-1}$ )

IR spectra showed a new band at (420-426)  $\text{cm}^{-1}$  the evidence for the coordination of metal to sulfur (M-S), this behavior may be attributed to the electron releasing of the amines, which forces high electron density towards the sulfur atoms, the  $\nu$  (M-N) was observed in the (465-523)  $\text{cm}^{-1}$  region [12]

In the adduct, the band corresponding to  $\nu$  (N-H) of the ethylene diamine (6,14,22,32 and 40) was observed at lower frequency (3211-3270)  $\text{cm}^{-1}$  (13), which indicates that it was shown in coordination with metal ions, as well as the band  $\nu$  (C=N) ring which was observed as (1479-1500)  $\text{cm}^{-1}$  which means the coordination of the donor atoms with the metal ions [14].

## Electronic spectral studies

The UV-visible spectra of ligand and their complexes of  $10^{-3}$  M solution in DMF were recorded; the results were listed in table (2). The UV-visible spectrum of the Fe(II) complex (1) gave absorption peak at (10309  $\text{cm}^{-1}$ ), which correspond to  ${}^5E \rightarrow {}^5T_2$  transition in tetrahedral geometry [15]. Complexes (2-8) shows absorption peaks at the range (10869-12820  $\text{cm}^{-1}$ ), which were assigned to  ${}^5T_2g \rightarrow {}^5Eg$  transition [16] in Octahedral geometry. Figure (13). The Co(II) complex (9) exhibited an absorption peak at (16666  $\text{cm}^{-1}$ ) region, which was assigned  ${}^4A_2(F) \rightarrow {}^4T_1(P)$  transition [17]. In tetrahedral configuration of this complex and the absence of  ${}^4A_2(F) \rightarrow {}^4T_2(F)$  and  ${}^4A_2(F) \rightarrow {}^4T_1(F)$ , are due to the sensitivity of the instrument used. Figure (14).

Complexes (10-16) show three absorption peaks at the range (9731-10394  $\text{cm}^{-1}$ ), (14367-16447  $\text{cm}^{-1}$ , 18726-22736  $\text{cm}^{-1}$ ) which were assigned to  ${}^4T_1g(F) \rightarrow {}^4T_2g(F)$ ,  ${}^4T_1g(F) \rightarrow {}^4A_2g(F)$  and  ${}^4T_1g(F) \rightarrow {}^4T_1g(p)$  transition in octahedral configuration [18] the Ni(II) complex (17) shows two absorption peaks at (8523  $\text{cm}^{-1}$ ) and (14670  $\text{cm}^{-1}$ ) which were assigned to  ${}^3T_1(F) \rightarrow {}^3A_2(F)$  and  ${}^3T_1(F) \rightarrow {}^3T_1(P)$  transition in tetrahedral geometry [15] respectively, the complexes (18-26) show three absorption peaks in the range (9611-10330  $\text{cm}^{-1}$ ), (14326-18096), (20567-25585  $\text{cm}^{-1}$ ), which were assigned  ${}^3A_2g(F) \rightarrow {}^3T_2g(F)$ ,  ${}^3A_2g(F) \rightarrow {}^3T_1g(F)$  and  ${}^3A_2g(F) \rightarrow {}^3T_1g(p)$  [19] in octahedral geometry. Figure (15) The Cu(II) complex (27) gave an absorption peak at (9083  $\text{cm}^{-1}$ ), which correspond to ( ${}^2T_2 \rightarrow {}^2E$ ) transition in a tetrahedral geometry [21] figure (16), the complexes (28-34) show broad peaks in the region (9960-12787  $\text{cm}^{-1}$ ), which was assigned to  ${}^2Eg \rightarrow {}^2T_2g$  transition which may be formed from the combination of three transitions  ${}^2B_1g \rightarrow {}^2A_1g$ ,  ${}^2B_1g \rightarrow {}^2B_2g$ , and  ${}^2B_1g \rightarrow {}^2Eg$  in octahedral geometry.

## Magnetic susceptibility measurements

The magnetic moments of the complexes Table(1) were measured at (25° C). The magnetic moments for Fe(II), Co(II), Ni(II) and Cu(II) complexes (1,9,17,27) are (1.75-4.95 B.M) suggesting tetrahedral geometry [15]. The low values of magnetic moments for complex (17 and 27) are due to antiferromagnetic interaction. The magnetic moments values of the other complexes (2-8,10-16,18-26,28-34) were in the range (1.65-5.13 B.M) in octahedral geometry [15]

## References

- 1- Shalin Kumav ,Durga Nath Dhav anit PN saxena (2009). Application of metal complexes of Schiff bases-A review, J.of scientific and industrial rescarch 68,181-187.
- 2- Percy, G.C and thornton D.A (1973) salicyl aldehyde complexes effects of metal ion substitution Ligand substitution and adduct formation on their in fra red spectra , J . Inorg .nucl .chem 35,2719-2726.
- 3- Leka, Z.B,Leovac V.m.Lukic S, Sabo T.J, Tri funovic S.R and Katalin M.S (2006) synthesis and phy sico- chemical characterization of new dithiocarbamate ligend and its complexes with copper (II), Nickel (II), and Palladium (II) , J. therm Anal and Cal 83.
- 4- Takagi, S. and Tanaki , Y.(1949) Preparation of Zinc alkyl dithiocarbamates, J.Pavm.so c. Jap 69-228.
- 5- Manohar, A.,Rumalingam, K. , Thiruneelakan elemn R,Bocell G and Righi L(2006) N-(2,hydroxyl ethyl) N-methyl dithiocarbamate complexes of nickel (II) with phosphorus donor ligands Anorg Altgchem 632 :461-464.
- 6- Ryo.K,TaKashi o and Todaoki, M(2006) structural and magnetic studies on anew mixed valence Cu(I)-Cu(II) octanucleav cluster with dithio carbamate derivative, polyhedron 25,2650-2654 .
- 7- Amna, S.A.Zidan (2001) Nickel(II) complexes containing mixed alkyl salicyl aldehyde and alkyl xanthiate as diethyl dithiocarbamate ligands ,synth . react Inorganic MET-ORG chem 31(3) ,457-4691.
- 8- Gruber, S.J.Harris and sinn, E.(1968) Metal complexes asLigands (1,2,3) bi and tri – nuclear complexes derived from metal complexes of tetra dentate salioyla dimens.J.Inorg.Nucl chem 30,(1805 -1830)
- 9- Gerry, W.J., (1971). The use of conductivity measurements inorganic solvents for characterization of coordination compounds , coord .chem .Rev . 7,8-122.
- 10- Srinivasan ,N; valarmathi. P; Thirumaran.s. and Ciattini.S.(2010). Synthesis and spectral studies on NiS<sub>4</sub>, NiS<sub>2</sub>PN, NiS<sub>2</sub>PN, NiS<sub>2</sub>P<sub>2</sub> chromophores= single –crystal x-ray structure of [ Ni(dbpdtc)<sub>2</sub>] (dbpdtc= benzyl(4-(benzyl amino ) phenyl) dithio carbamate). Trans metchem.,35,815-819.
- 11- Serrano,J.L.;García.L.; pefez. J.; pefez E.; sañchez .G.; García .J.;LoPez .G.;Garclá.G and Molins. E.(2003). New dithiocarbamate and xanthate complexes of nikel (II) with iminoposphines .Inorg chim Acta.,355,33-40.
- 12- Raya,I.,Baba.I.and Yamin.B.,(2006).New Mixed ligands complexes of samarium(III) with dithiocarbamates and 1,10-phenanthroline.Malaysia.J.Analy.Sci.,10(1) 93-98.
- 13- Montagner,D.: Marzano.C.: and Gandin.V.(2011).synthesis,characterization and cytotoxic activity of palladium (II) dithiocarbamate complexes with a,x-diamines.Inorg chim Acta376,574-580.
- 14- Ceraldo, M.de Lima,Daniele C.Menezes,Camila A.Cavalcanti,Jaqueline A.F.dos Santos, Isabella P.Ferreira,Eucler B.paniago,James L.Wardell a,Solange M.S.V.Wardell,Klaus

- Krambrock, Isolda C. Mendes, and Heloisa Beradlo (2011), Journal of Molecular Structure., 988, 1-8.
- 15- Nicholls, D. (1973). "The chemistry of Iron, Cobalt and Nickel" Pergamon Press, Oxford, 1<sup>st</sup> Ed., pp. 1037, 1087, 1088, 1090, 1091, 1093, 1151, 1154.
- 16- Coucouvanis, D. and Fackler, J.P. (1967). Square-planar sulfur complexes. VI. Reaction of bases with xanthate, dithiocarbamates, and dithiolates of nickel(II). *Jr. Inorg. Chem.*, 6, 2047-2053.
- 17- Siddiqi, K.S. and Nishat, N. (2000). Synthesis and characterization of succinimide and phthalimide dithiocarbamate and their complexes with some transition metal ions. *Synth. Reac. Inorg. Met-Org. Chem.*, 30(8) 1505-1518.
- 18- Martell, A.E. (1971). "Coordination Chemistry", Van Nostrand Reinhold, New York., p.1.
- 19- Singh, N.; Singh, N.K. and Kaw, C. (1989) Synthetic and Spectroscopic studies of xanthate-bridged hetero bimetallic complexes containing diamagnetic and paramagnetic metal ions. *Bull. Chem. Soc. (Jpn)*, 62, 3328-3333.
- 20- Cookson, J.; Emma, A.L.E; John, P.M, Christopher, J.S.; Rowena, L.P.; Andrew, R.C, Michael G.B.D., and Paul D. (2010). Metal directed assembly of large dinuclear copper (II) dithiocarbamate macrocyclic complexes. *Inorg chim Acta.*, 363, 1195-1203.
- 21- Lever, A.B.P. (1984). "Inorganic Electronic Spectroscopy" (2<sup>th</sup> ed), Elsevier Amsterdam, PP357.

**Table (1) : Analytical and some physical properties of the prepared complexes**

No	Compound	Color	M.P(c)	Molar conductivity $\Omega^{-1}.cm^2.mol^{-1}$	%M	%yield	$M_{eff}$ B.M
L	$C_7H_7N_2S_2Na$	Pale yellow	100	-----	-----	75	-----
1	$[Fe(4-ABdtc)_2]$	Light brown	280*	21.6	12.426 (13.226)	78	4.95
2	$[Fe(4-ABdtc)_2(py)_2]$	Greenolive	210*	7.44	8.774 (9.624)	72	4.95
3	$[Fe(4ABdtc)_2(isoQui)_2]$	brown	240*	4.7	7.606 (8.0206)	51	5.05
4	$[Fe(4-ABdtc)_2(\gamma-pico)_2]$	Light brown	236	4.6	8.0477 (9.0177)	53	5.09
5	$[Fe(4-ABdtc)_2(3,5-Lut)_2]$	orang	294	10.9	8.223 (8.773)	63	4.85
6	$[Fe(4-ABdtc)_2(en)]$	Reddish brown	298	2.3	11.336 (11.926)	54	4.96
7	$[Fe(4-ABdtc)_2(1,10-phen)]$	red	280	8.3	9.186 (9.276)	68	5.13
8	$[Fe(4-ABdtc)_2(2,2bipy)]$	Light brown	70	1.7	9.654 (8.0654)	59	5.06
9	$[Co(4-ABdtc)_2]$	gray	248*	26.4	12.864 (13.854)	58	4.22
10	$[Co(4-ABdtc)_2(py)_2]$	brown	240*	11.58	9.411 (10.101)	70	3.95
11	$[Co(4-ABdtc)_2(isoQui)_2]$	gray	260	10.2	7.652 (8.622)	55	3.96
12	$[Co(4-ABdtc)_2(\gamma-pico)_2]$	Dark brown	148	7.4	7.865 (9.635)	50	4.00
13	$[Co(4-ABdtc)_2(3,5-Lut)_2]$	gray	270	4.3	8.862 (9.212)	50	3.85
14	$[Co(4-ABdtc)_2(en)]$	Dark brown	260*	7.6	11.401	63	4.39

15	[Co(4-ABdtc) <sub>2</sub> (1,10-phen)]	brown	266	16.77	(12.501) 8.698 (9.738)	60	3.86
16	[Co(4-ABdtc) <sub>2</sub> (2,2bipy)]	brown	160*	2.8	9.817 (10.137)	65	3.91
17	[Ni(4-ABdtc) <sub>2</sub> ]	Light green	220	7.2	13.305 (13.805)	85	2.88
18	[Ni(4-ABdtc) <sub>2</sub> (py) <sub>2</sub> ]	Dark gray	260*	7.8	9.78 (9.950)	61	3.69
19	[Ni(4-ABdtc) <sub>2</sub> (isoQui) <sub>2</sub> ]	green	264*	11.2	8.337 (8.587)	51	3.35
20	[Ni(4-ABdtc) <sub>2</sub> (γ-pico) <sub>2</sub> ]	Green olive	250*	3.5	8.839 (9.599)	51	3.05
21	[Ni(4-ABdtc) <sub>2</sub> (3,5-Lut) <sub>2</sub> ]	green	244*	4.2	8.088 (9.178)	54	2.91
22	[Ni(4-ABdtc) <sub>2</sub> (en)]	gray	212	9.1	11.347 12.457	68	2.83
<b>No</b>	<b>Compound</b>	<b>Color</b>	<b>M.P(c)</b>	<b>Molar conductivity Ω<sup>-1</sup>.cm<sup>2</sup>.mol<sup>-1</sup></b>	<b>%M</b>	<b>%yield</b>	<b>M<sub>eff</sub> B.M</b>
23	[Ni(4-ABdtc) <sub>2</sub> (1,10-phen)]	green	240*	2.8	9.072 (9.702)	63	2.92
24	[Ni(4-ABdtc) <sub>2</sub> (2,2bipy)]	gray	240	1.7	9.776 (10.096)	62	3.03
25	[(CH <sub>3</sub> ) <sub>4</sub> N][Ni(4-ABdtc) <sub>3</sub> ]	Light green	252*	70.15	7.627 (8.607)	52	2.96
26	[(C <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> N][Ni(4-ABdtc) <sub>3</sub> ]	Dark green	266*	68.2	6.37 (7.140)	51	2.87
27	[Cu(4-ABdtc) <sub>2</sub> ]	brown	268	11.5	13.94 (14.780)	71	1.75
28	[Cu(4-ABdtc) <sub>2</sub> (py) <sub>2</sub> ]	Dark brown	260*	8.26	10.058 (10.808)	68	1.65
29	[Cu(4-ABdtc) <sub>2</sub> (isoQui) <sub>2</sub> ]	gray	290*	10.6	8.163 (9.233)	53	1.80
30	[Cu(4-ABdtc) <sub>2</sub> (γ-pico) <sub>2</sub> ]	brown	288	16.8	9.452 (10.312)	50	2.40
31	[Cu(4-ABdtc) <sub>2</sub> (3,5-Lut) <sub>2</sub> ]	Dark brown	310	2.5	8.733 (9.863)	62	1.83
32	[Cu(4-ABdtc) <sub>2</sub> (en)]	brown	298	2.8	12.651 (13.351)	80	1.66
33	[Cu(4-ABdtc) <sub>2</sub> (1,10-phen)]	brown	242	2.00	9.492 (10.422)	70	1.70
34	[Cu(4-ABdtc) <sub>2</sub> (2,2bipy)]	Dark brown	200	3.1	10.041 (10.481)	51	1.75
35	[Zn(4-ABdtc) <sub>2</sub> ]	Of-white	254	4.16	14.253 (15.143)	74	Dia
36	[Zn(4-ABdtc) <sub>2</sub> (py) <sub>2</sub> ]	Of-white	220*	6.51	10.516 (11.086)	64	Dia
37	[Zn(4-ABdtc) <sub>2</sub> (isoQui) <sub>2</sub> ]	Of-white	204	6.17	8.615 (9.185)	51	Dia
38	[Zn(4-ABdtc) <sub>2</sub> (γ-pico) <sub>2</sub> ]	Of-white	270*	3.8	9.729 (10.120)	55	Dia
39	[Zn(4-ABdtc) <sub>2</sub> (3,5-Lut) <sub>2</sub> ]	Of-white	282	1.3	9.89 (10.120)	55	Dia
40	[Zn(4-ABdtc) <sub>2</sub> (en)]	Of-white	96	5.8	12.844 (13.684)	58	Dia
41	[Zn(4-ABdtc) <sub>2</sub> (1,10-phen)]	Of-white	280*	10.16	9.741 (10.691)	60	Dia
42	[Zn(4-ABdtc) <sub>2</sub> (2,2bipy)]	Of-white	100	7.1	10.527	53	Dia

\* = Degree of disintegration

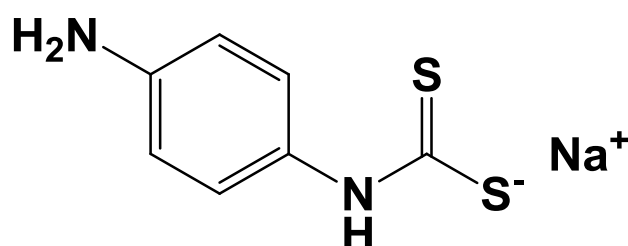
**Table (2): IR bands (cm<sup>-1</sup>) and electronic spectral data of ligand and prepared complexes**

No	Compound	U.V band(cm <sup>-1</sup> )	IR Spectra(cm <sup>-1</sup> )				
			$\nu$ (C-N)	$\nu$ (C-S)	$\nu$ (N-H)	$\nu$ (M-N)	$\nu$ (M-S)
L	C <sub>7</sub> H <sub>7</sub> N <sub>2</sub> S <sub>2</sub> Na	----	1448	1007	3350	----	----
1	[Fe(4-ABdtc) <sub>2</sub> ]	10309	1504	915	3332	----	420
2	[Fe(4-ABdtc) <sub>2</sub> (py) <sub>2</sub> ]	11095	1500	975	3296	472	420
3	[Fe(4ABdtc) <sub>2</sub> (isoQui) <sub>2</sub> ]	10869	1500	960	3335	493	418
4	[Fe(4-ABdtc) <sub>2</sub> ( $\gamma$ -pico) <sub>2</sub> ]	10940	1502	1005	3332	467	418
5	[Fe(4-ABdtc) <sub>2</sub> (3,5-Lut) <sub>2</sub> ]	11467	1500	990	3336	510	424
6	[Fe(4-ABdtc) <sub>2</sub> (en)]	12820	1496	984	3413	467	418
7	[Fe(4-ABdtc) <sub>2</sub> (1,10-phen)]	11494	1495	900	3319	475	420
8	[Fe(4-ABdtc) <sub>2</sub> (2,2bipy)]	11490	1500	975	3309	474	432
9	[Co(4-ABdtc) <sub>2</sub> ]	16666	1514	915	3327	----	420
10	[Co(4-ABdtc) <sub>2</sub> (py) <sub>2</sub> ]	9731,15324,21647	1508	930	3437	515	418
11	[Co(4-ABdtc) <sub>2</sub> (isoQui) <sub>2</sub> ]	9850, 16367, 18726	1506	945	3319	465	424
12	[Co(4-ABdtc) <sub>2</sub> ( $\gamma$ -pico) <sub>2</sub> ]	10394, 16447, 21008	1508	960	3278	492	418
13	[Co(4-ABdtc) <sub>2</sub> (3,5-Lut) <sub>2</sub> ]	9523, 14367, 1879	1500	945	3276	450	418
14	[Co(4-ABdtc) <sub>2</sub> (en)]	10271, 15343, 22736	1490	900	3510	465	418
15	[Co(4-ABdtc) <sub>2</sub> (1,10-phen)]	9723, 14705, 18518	1485	975	3332	455	418
16	[Co(4-ABdtc) <sub>2</sub> (2,2bipy)]	10295, 15217, 21645	1500	900	3230	455	418
17	[Ni(4-ABdtc) <sub>2</sub> ]	8523, 14670	1522	915	3319	----	420
18	[Ni(4-ABdtc) <sub>2</sub> (py) <sub>2</sub> ]	9611, 18867, 24509	1518	920	3455	510	418
19	[Ni(4-ABdtc) <sub>2</sub> (isoQui) <sub>2</sub> ]	9863, 18796, 24390	1475	947	3319	426	418
20	[Ni(4-ABdtc) <sub>2</sub> ( $\gamma$ -pico) <sub>2</sub> ]	9792, 18796, 24752	1500	974	3315	426	418
21	[Ni(4-ABdtc) <sub>2</sub> (3,5-Lut) <sub>2</sub> ]	10240,18096,24752	1494	974	3319	426	418
22	[Ni(4-ABdtc) <sub>2</sub> (en)]	9865, 18796, 20576	1479	945	3336	426	420
23	[Ni(4-ABdtc) <sub>2</sub> (1,10-phen)]	10330, 18939,23923	1496	949	3334	467	418
24	[Ni(4-ABdtc) <sub>2</sub> (2,2bipy)]	9990, 18796, 24390	1500	930	3319	450	420
25	[(CH <sub>3</sub> ) <sub>4</sub> N][Ni(4-ABdtc) <sub>3</sub> ]	9730, 14326, 25585	1514	947	3319	450	418
26	[(C <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> N][Ni(4-ABdtc) <sub>3</sub> ]	10100, 18656, 24509	1500	947	3319	465	418
27	[Cu(4-ABdtc) <sub>2</sub> ]	9083	1512	900	3346	----	426
28	[Cu(4-ABdtc) <sub>2</sub> (py) <sub>2</sub> ]	11702	1508	915	3325	465	418
29	[Cu(4-ABdtc) <sub>2</sub> (isoQui) <sub>2</sub> ]	12263	1490	919	3332	450	420
30	[Cu(4-ABdtc) <sub>2</sub> ( $\gamma$ -pico) <sub>2</sub> ]	12787	1495	975	3437	472	418
31	[Cu(4-ABdtc) <sub>2</sub> (3,5-Lut) <sub>2</sub> ]	10902	1508	960	3334	495	418



32	[Cu(4-ABdtc) <sub>2</sub> (en)]	12642	1496	930	3344	519	418
33	[Cu(4-ABdtc) <sub>2</sub> (1,10-phen)]	11893	1502	965	3335	450	420
34	[Cu(4-ABdtc) <sub>2</sub> (2,2bipy)]	9960	1500	915	3309	493	420
35	[Zn(4-ABdtc) <sub>2</sub> ]	30487, 37313	1514	960	3313	----	418
36	[Zn(4-ABdtc) <sub>2</sub> (py) <sub>2</sub> ]	37313	1502	975	3338	484	418
37	[Zn(4-ABdtc) <sub>2</sub> (isoQui) <sub>2</sub> ]	25125, 37073	1492	984	3336	459	420
38	[Zn(4-ABdtc) <sub>2</sub> (γ-pico) <sub>2</sub> ]	30487, 37313	1496	984	3313	450	420
39	[Zn(4-ABdtc) <sub>2</sub> (3,5-Lut) <sub>2</sub> ]	3030, 3737	1492	984	3332	459	420
40	[Zn(4-ABdtc) <sub>2</sub> (en)]	37313	1500	984	3319	459	418
41	[Zn(4-ABdtc) <sub>2</sub> (1,10-phen)]	30864, 26737	1508	956	3319	455	418
42	[Zn(4-ABdtc) <sub>2</sub> (2,2bipy)]	35211	1496	984	3330	459	418

### Suggest structures



sodium 4-aminobenzenedithiocarbamate  
(4-ABdtc)

Figure (1) : The predicate structure of the ligand

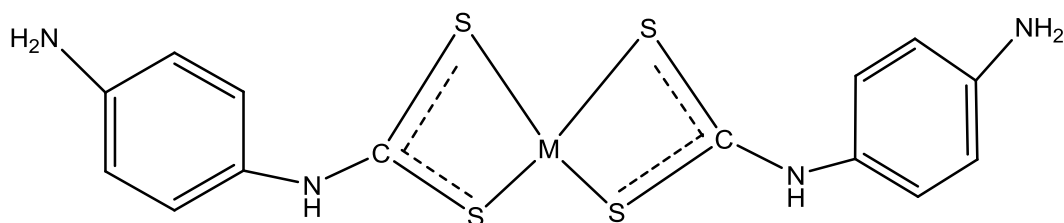
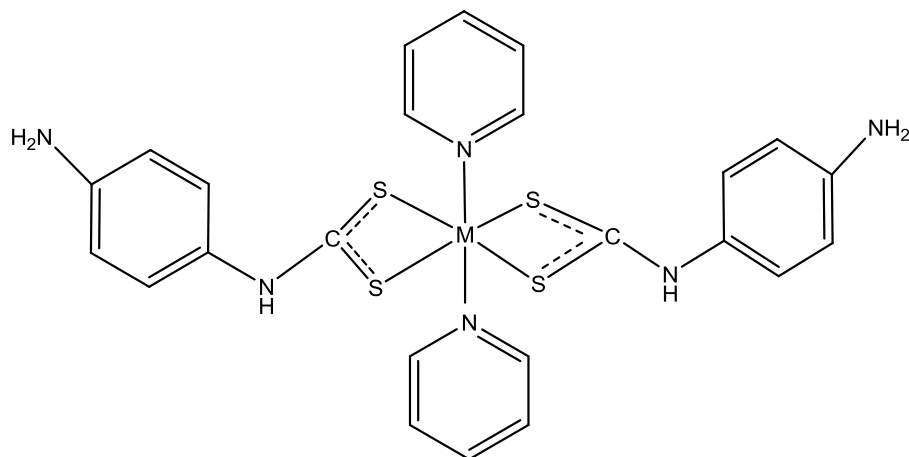


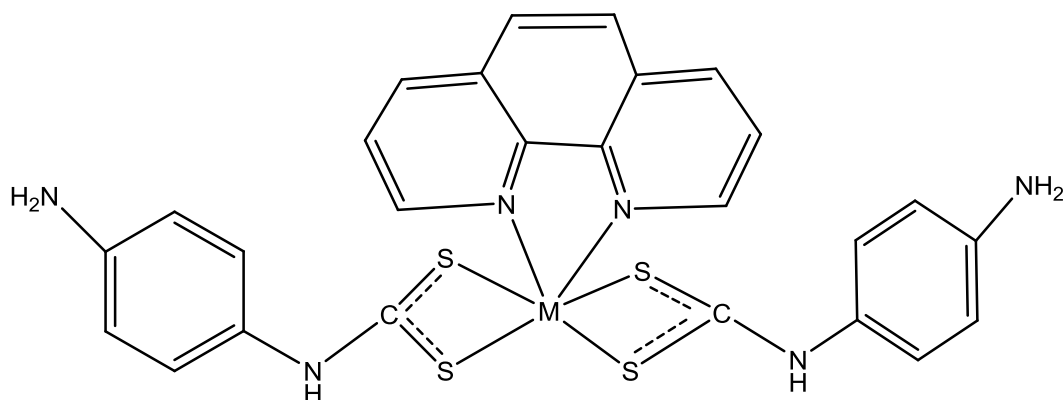
Figure (2) : The predicate structure of the complex (1,9,17,27,35)  
M=Fe(II), Co(II), Ni(II), Cu(II), Zn(II)



**Figure (3) : The predicate structure of the complex ( 2-5, 10-13,18-21, 28-31, 36-39)**

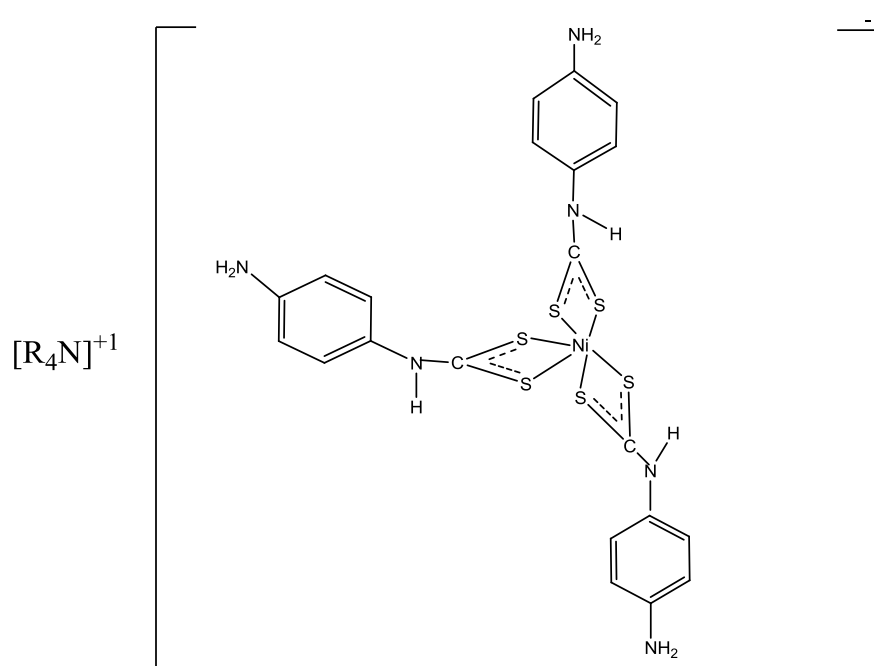
**M= Fe(II), Co(II),Ni(II),Cu(II),Zn(II)**

**n= Number of nitrogen bases =2 when X= Py, $\gamma$ -Pic,isoquinoline ,3,5-lutidine**

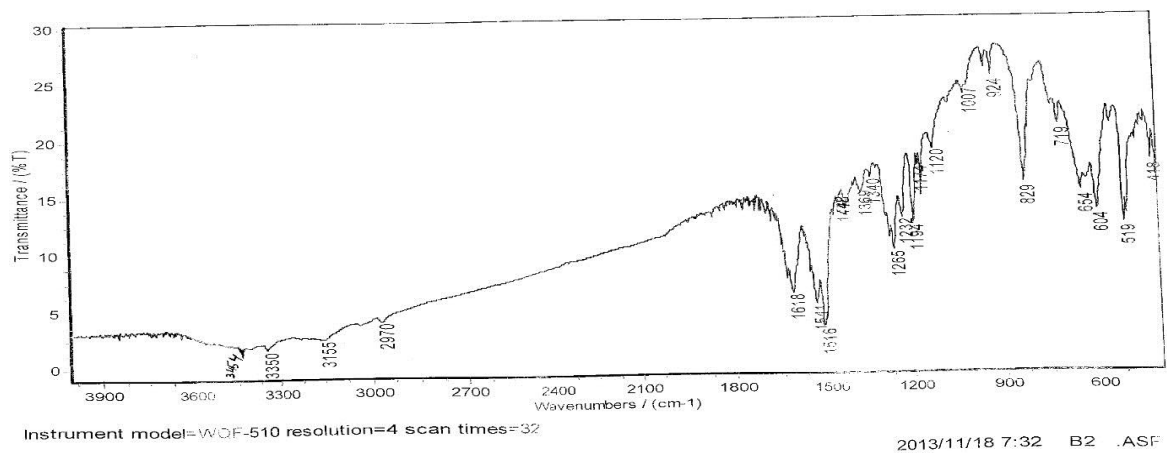


**Figure (4) : The predicate structure of the complex ( 6-8,14-16,22-24,32-34,40-42)**

**M= Fe(II), Co(II),Ni(II),Cu(II),Zn(II) n= Number of nitrogen bases =1when x=1,10-phenanthroline, en, 2,2bipy**



**Figure(5) : The predicate structure of the complex of type ( R)<sub>4</sub>N[Ni(PABdtc)<sub>3</sub>]  
R= methyl,ethyl**



**Figure (6): FTIR Spectrum of P-phenylene diamine dithiocarbamate ligand**

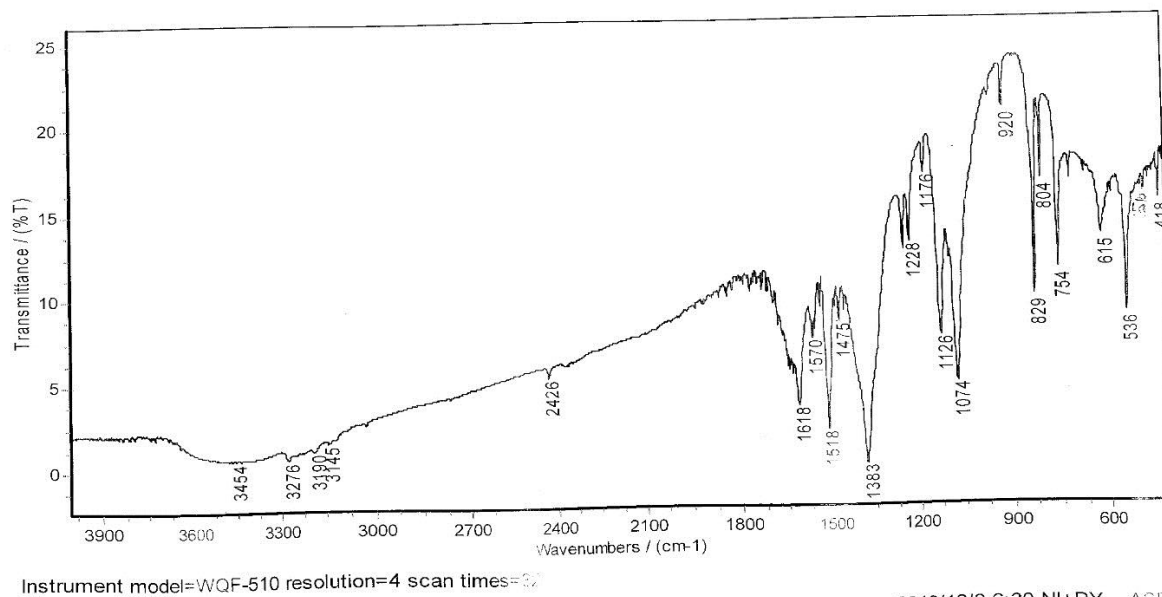
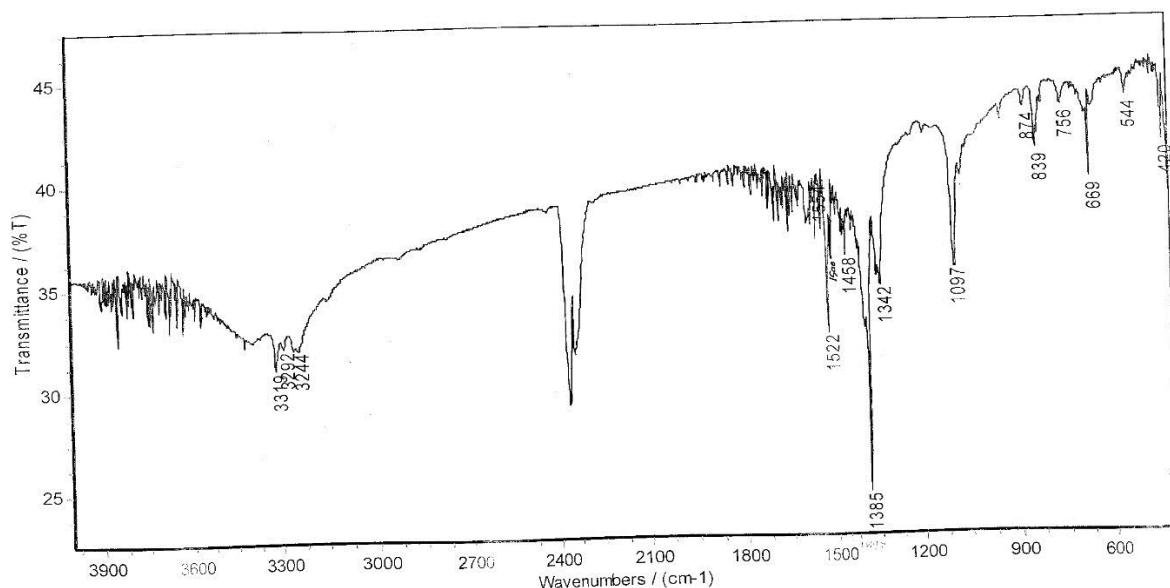


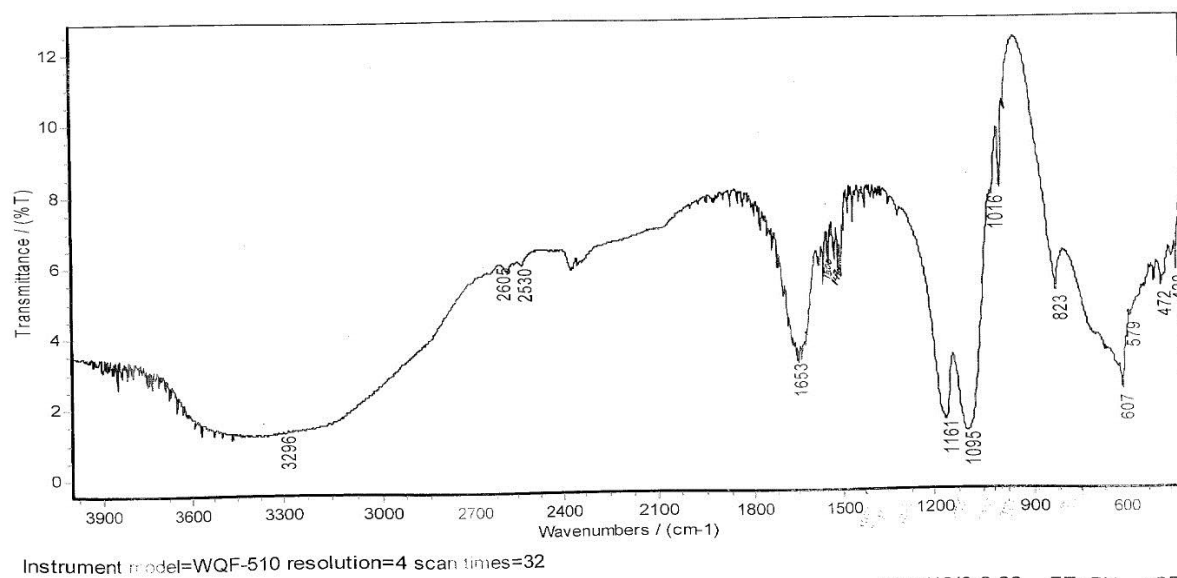
Figure (7): FTIR Spectrum of  $[\text{Ni}(4\text{-ABdtc})_2(\text{py})_2]$  complex



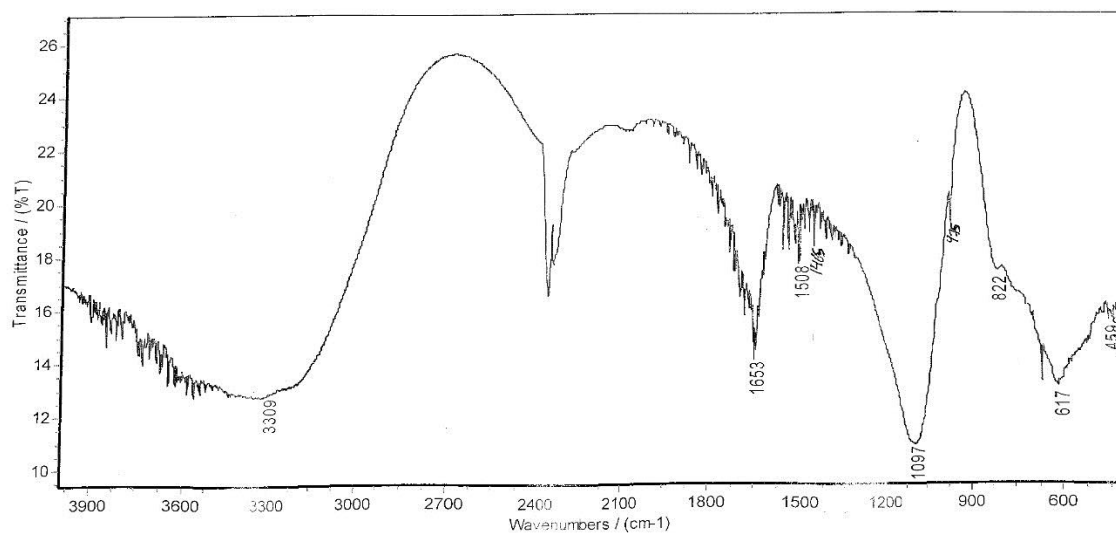
Instrument model=WQF-510 resolution=4 scan time=32

2013/12/23 7:16 NI+BIP .ASF

**Figure (8): FTIR Spectrum of  $[\text{Ni}(4\text{-ABdtc})_2(2,2'\text{bipy})]$  complex**



**Figure (9): FTIR Spectrum of [ Fe(4-ABdtc)<sub>2</sub>(py)<sub>2</sub>] complex**

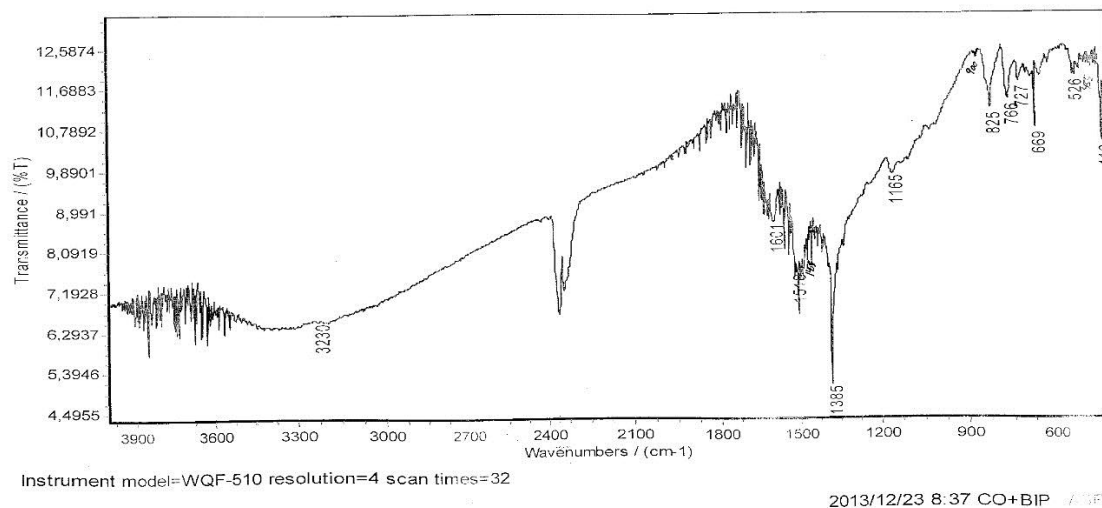


Instrument model=WQF-510 resolution=4 scan times=32

2013/12/23 8:33 FE+BIP .ASF

**Figure (10): FTIR Spectrum of [Fe(4-ABdtc)<sub>2</sub>(2,2bipy)] complex**





**Figure (11): FTIR Spectrum of [Co(4-ABdtc)<sub>2</sub>(2,2bipy)]complex**

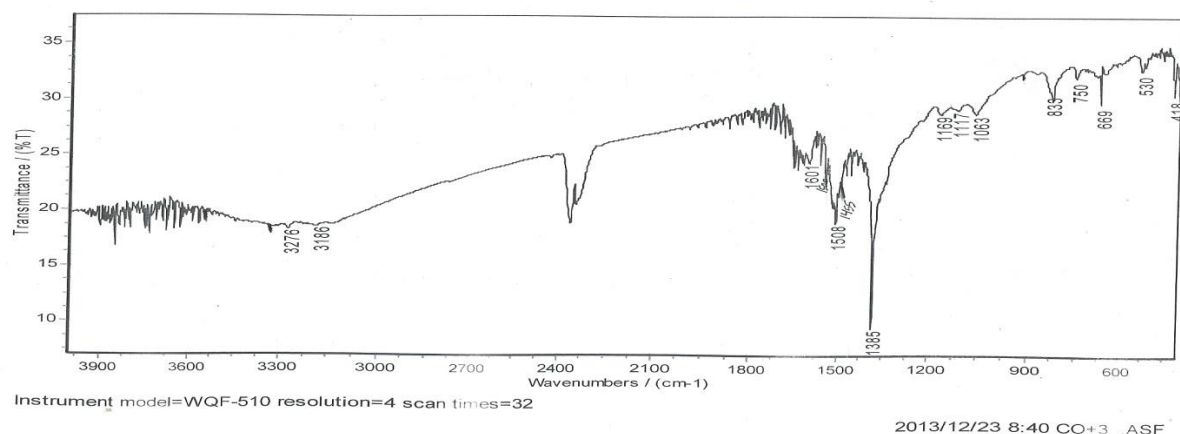


Figure (12): FTIR Spectrum of [Co(4-ABdtc)<sub>2</sub>(3,5-Lut)<sub>2</sub>] complex

Data Set: p38 - RawData - F:\omar\new\p38.spc

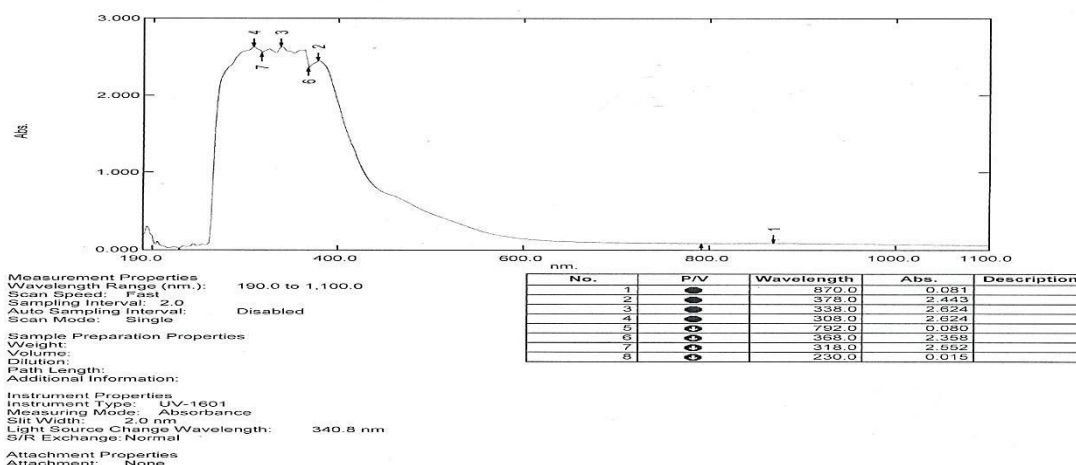


Figure (13): Electronic Spectrum of [Fe(4-ABdtc)<sub>2</sub>(1,10-phen)] complex

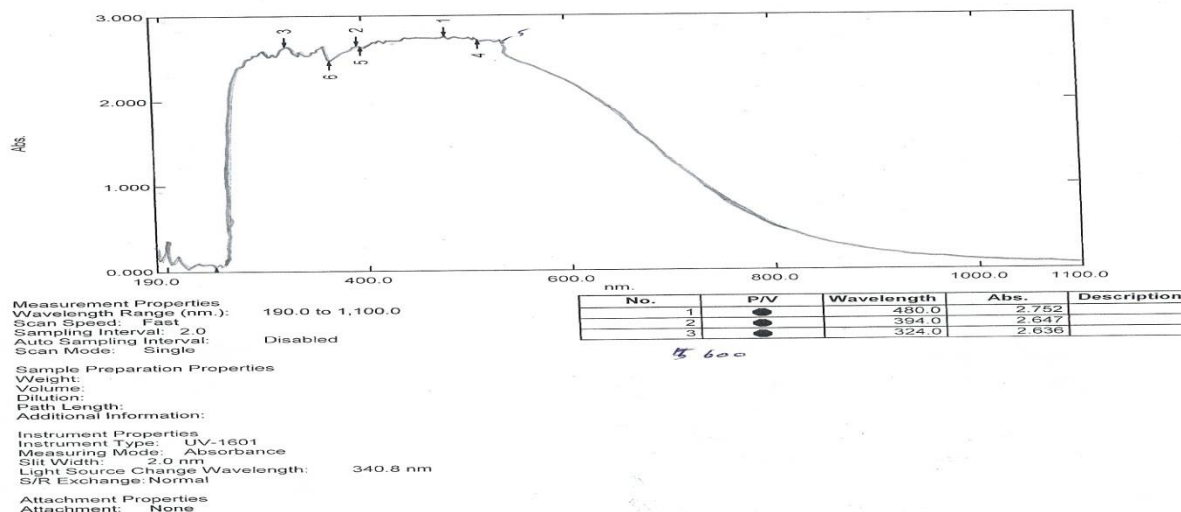
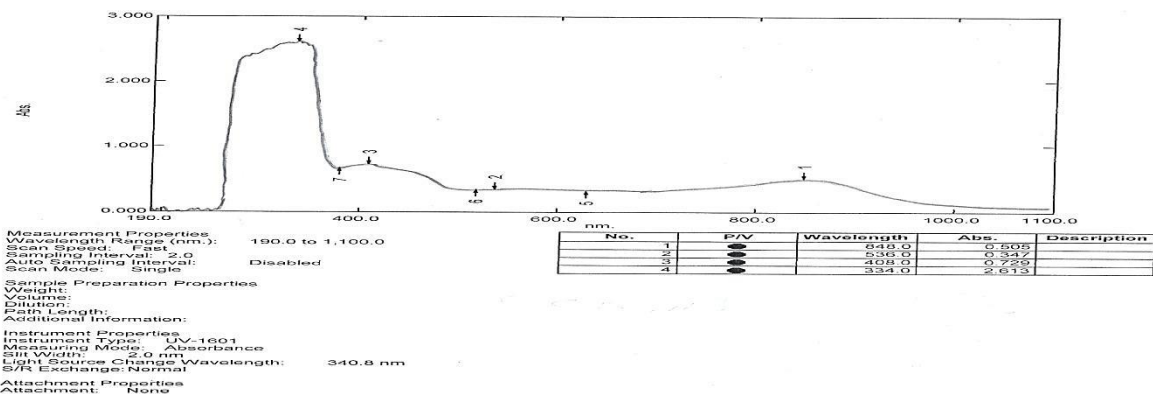
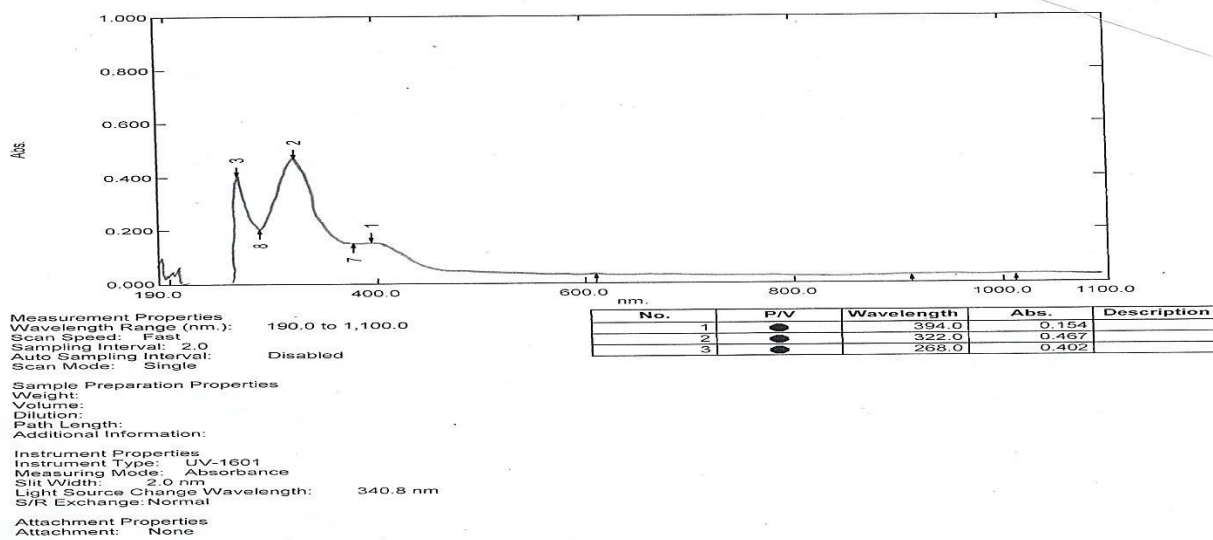


Figure (14): Electronic Spectrum of [Co(4-ABdtc)<sub>2</sub>] complex



**Figure (15): Electronic Spectrum of [(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>N][Ni(4-ABdtc)<sub>3</sub>] complex**



**Figure (16): Electronic Spectrum of [Cu(4-ABdtc)<sub>2</sub>] complex**