Journal of Natural Sciences Research www.iiste.org
ISSN 2224-3186 (Paper) ISSN 2225-0921 (Online)
Vol.3, No.10, 2013

Synthesis and Identification of Nickel (ll) , Cobalt (ll) and Copper (ll) Complexes with the Organic Reagent (Sodium – 1 – Amino – 9,10 – Dioxo – 4 – Phenylamin – Anthracene – 2 – Sulphonate)

Jassem Mohamad Abd Al Hassien
University of Babylon , College of science , Department of Chemistry
E-Mail : mjaseem67@yahoo.com*

Abstract
The complexes of Nickel (ll) , Cobalt (ll) and Copper (ll) were synthesized by using Sodium – 1 – Amino – 9,10 – Dioxo – 4 – Phenylamin – Anthracene – 2 – Sulphonate , acid blue – 25 , (AB25) reagent as a ligand . They were characterized by many techniques such as the element analysis , IR spectroscopy and UV.VIS. spectroscopy . Their physical properties such as electric conductivity and magnatic properties , were determind . It was found that Nickel (ll) complex has diamagnetic properties , whereas Cobalt (ll) and Copper (ll) complexes have paramagnetic properties . Cobalt complex did not have any conductivity , whereas the ligand , Nickel (ll) complex and Copper (ll) complex have good conductivity . The formula of the complexes under this research were detected by using the mole ratio method which lead to the formation of (1:1) metal : ligand formula for Nickel (ll) and Copper (ll) complexes , whereas Cobalt (ll) complex was (1:2) metal : ligand formula . In all the complexes the coordination was through O and N atoms of the oxo sulfate and amine groups . the suggested geometrical shapes of the complexes were the squar pyramidal shape for Nickel (ll) and Copper (ll) complexes and octahedral for Cobalt (ll) complex .
Keywords : Acid Blue – 25 , Ni (ll) complex , Cu (ll) complex , Co (ll) complex , IR spectroscopy , geometrical shapes

1 – Introduction

The high molecular weight coordination complexes have a wide importance in the field of clinical and analytical chemistry in recent days that because of their high stability and their useful utilization (Loo & Hu 1994 , Sido & Brown 1965 , Sony *et al.* 2004) . There are many antibiotics react with many transition metal ions to form stable complexes such as ciprofloxacin which reacts with copperic ion to form stable chelate complex (Wn *et al.* 2003) . From another side , there are many ligands such as 8 – hydroxyl quinolin , oxalate and carbazate used to form complexes with many heavy metal ions which can be act as antitoumer drugs (Rashan *et al.* 1990) . Many recrnt studies found that the complexes have antibiotic activity more than the free ligands (Sadik *et al.* 2003) . In industrial fields , the formation of complexes used in the purification of petroleum (Salih & Sheriff 1990) . Nickel , Cobalt and Copper are within the 25 essential metal ions that are required by most of biological systems . Many organisms such as Lactobacilli that their ribonucleotide reductase uses cobalt as a cofactor . nickel appears to be much more extensively utilized by anaerobic bacteria . Copper laccase enzyme catalyses the oxidation of uroshiol in the production of Japanese Lacquer (Crichton 2008) . Jasem had prepared the complexes of Pb (IV) , Cd (ll) and Fe (lll) by using the reagent that used in this research and he found that these complexes had good stability (Husain 2012) . The most stable Co(ll) complexes have the octahedral coordination and Ni(ll) complexes have the squar planar coordination while Cu(ll) complexes have the tetrahedral coordination (Al-Rasaq 1984) . In biochemistry , Biuret test , cupric ion has been used to detect and value the amount of protein in its basic solutions by the coordination via its amino groups to form violet complex (Yasser 2004) . Cytochrome oxidase (cytochrome a_3 + a) consiste of copper in addition to iron and porphyrin to establish its biological role of transporting the electrons and oxidative phosphorylation in organisms (Lehninger 1975 , Kabsh & Asos 1988) . Cobalt is an essential element for the functioning of many vital processes such as the processes of blood formation , stimulation of hemoglobin synthesis , the functioning of vitamins , the functioning of enzymes , the functioning of hormones , influence on metabolism of vitamins (ascorbic acid and B12) and the synthesis of a number of hormomes , neurotransmitters , bile acids and DNA (Ahmad 1986 , Grahovav *et al.* 2006) .

2 – Prartical Part

Spectral and Physical Measurments :

IR spectrum were recorded for the ligand and the complexes by using FTIR – 84005 Shimadzu Specroscopy with KBr discs in the rang (400 – 4000) cm^{-1} .
UV.VIS. spectrum were recorded for the aqeous solutions of the ligand and for the ethanolic solutions of the complexes by using UV – 1650 PC Shimadzu Specroscopy with quartz cells .

Element analysis was established by using EURO EA (Element Analyzer) and Shimadzu – AA – 160 Atomic Absorption – Flame Emission Spectrosphotometer .
Magnatic susceptibility measurmeants where established by using MSB – MKI Magnatic Susceptibility Measurment Balance .
The electric conductivity for the solutions were measured by using INOL AB 740 Potentiometer .

Materials :

All the materials which were used in this research were so sensitive to air and moisture that they have been kept in dry containers .

The water used was double distilled water .

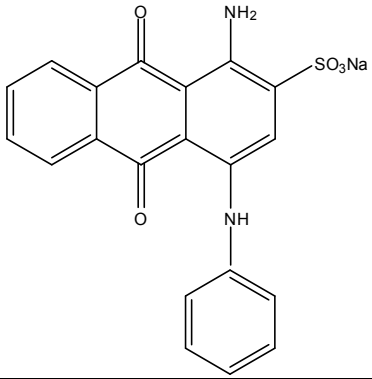
Nickel (ll) , Cobalt (ll) and copper (ll) solutions (0.001 M) were prepared from theres chloride salts .

All the reagent were of high purity , they get from BDH and Fluka companies .

Sodium nitrate used to prepare the background electrolytic solutions .

The used ligand has the commercial name ; acid blue 25 (AB 25) . Table (1) shows some properties of the ligand.

Table (1) some properties of the ligand :

Scientific name	Sodium – 1 – amino – 9,10 – dioxo – 4 – phenylamin anthracin – 2 - sulphonate
Chemical structure	
Symbol	AB25
Commercial name	Acid Blue – 25
Molecular formula	C20H13N2O5SNa
Molecular weight	416.38
Physical state	Solid powder
apperance	blue

Preparation the Complexes :

Preparation of Ni (ll) Complex :

0.001 moles (0.237 g) of nickel chloride (NiCl2.6H2O) , dissolved in 20 ml of distilled water , and 0.001 moles (0.417 g) of the ligand (AB 25) , dissolved in 10 ml of distilled water , mixed together and 2ml of 10% NaOH added to the mixture . After heating to 70 ^{o} c for 30 minutes agreen – blue precipitate was formed , separated by filtaration and washed by ethanol then dried at 50^{o} c . The product percentage was 70% .

Preparation of Co (ll) Complex :

0.001 moles (0.237 g) of cobalt chloride (CoCl2.6H2O) , dissolved in 20 ml of distilled water , and 0.001 moles (0.417 g) of the ligand (AB 25) , dissolved in 10 ml of distilled water , mixed together and 2ml of 10% NaOH added to the mixture . After heating to 70 ^{o} c for 30 minutes agreen – blue precipitate was formed , separated by filtaration and washed by ethanol then dried at 50^{o} c . The product percentage was 65 % .

Preparation of Cu (ll) Complex :

0.001 moles (0.170 g) of cobalt chloride (CuCl2.2H2O) , dissolved in 20 ml of distilled water , and 0.001 moles (0.417 g) of the ligand (AB 25) , dissolved in 10 ml of distilled water , mixed together and 2ml of 10% NaOH added to the mixture . After heating to 70 ^{o} c for 30 minutes agreen – blue precipitate was formed , separated by filtaration and washed by ethanol then dried at 50^{o} c . The product percentage was 67 % .

Determination the Maximum Wavelength (λ_{max}) :

10^{-3} M solutions of the ligand and complexes were prepared , UV.VIS. spectral scanning was obtained , λ_{max} was recorded for each solution . The figures (1-4) shows the electronic spectra of ligand and its complexes . Table (1) shows the λ_{max} values of the ligand and its complexe

Table (2) electronic spectra of the ligand and its complexes (Buhlmann & Affolter 2000) :

compound	nm)(λ_{max}	Assig.	$_{max}$(L.mol^{-1}.cm^{-1}) ξ
AB25	280 390 590	$\pi \rightarrow \pi^*$ $\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$	2900 100 330
AB25-Ni	260 380 640	$\pi \rightarrow \pi^*$ $\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$	2200 200 600
AB25-Co	280 380 635	$\pi \rightarrow \pi^*$ $\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$	2000 150 600
AB25-Cu	285 380 633	$\pi \rightarrow \pi^*$ $\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$	2150 200 350

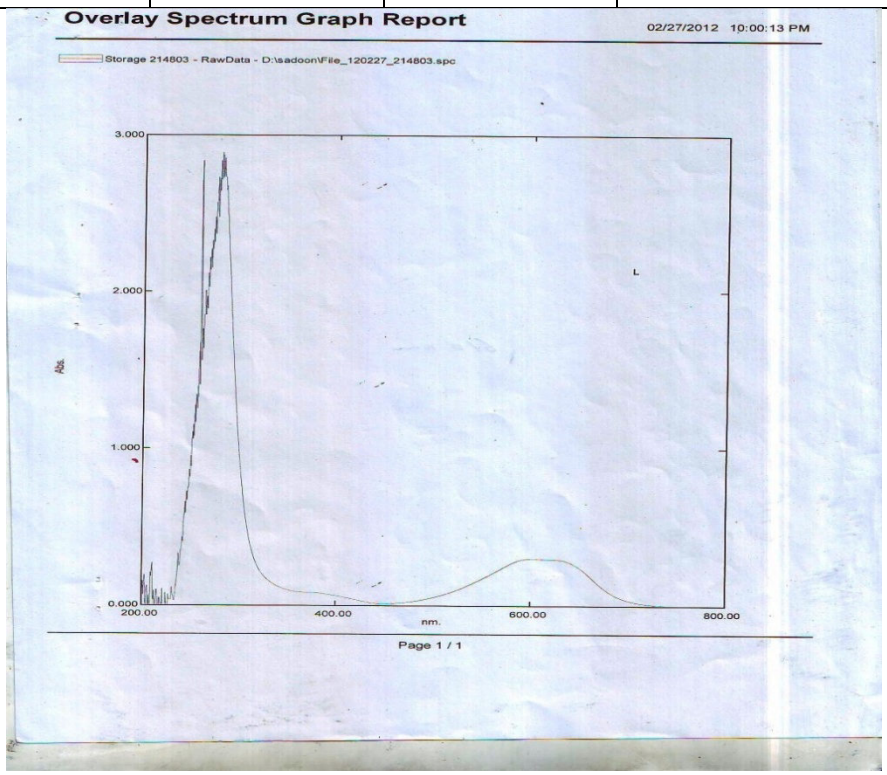


Figure (1) : electronic spectra of AB25 ligand

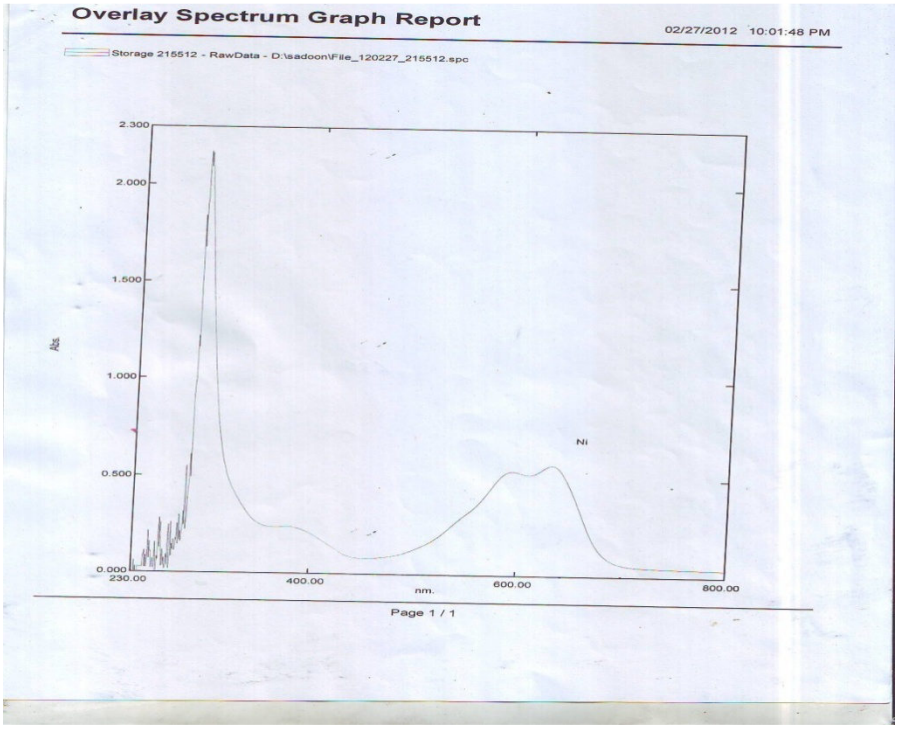


Figure (2) electronic spectra of Ni – AB25 complex

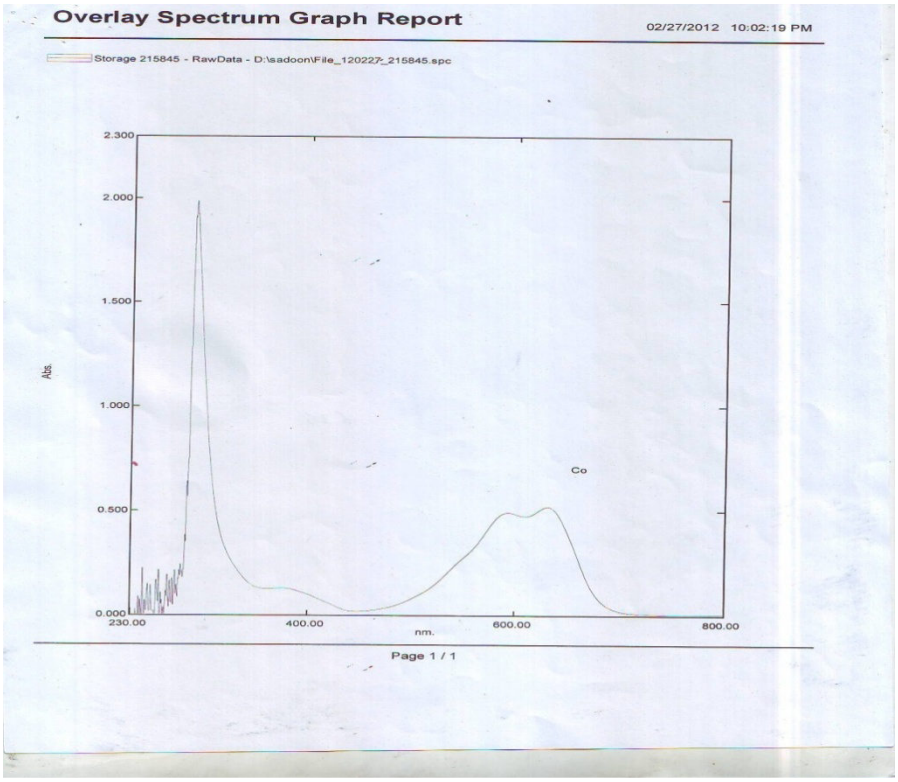


Figure (3) electronic spectra of Co – AB25 complex

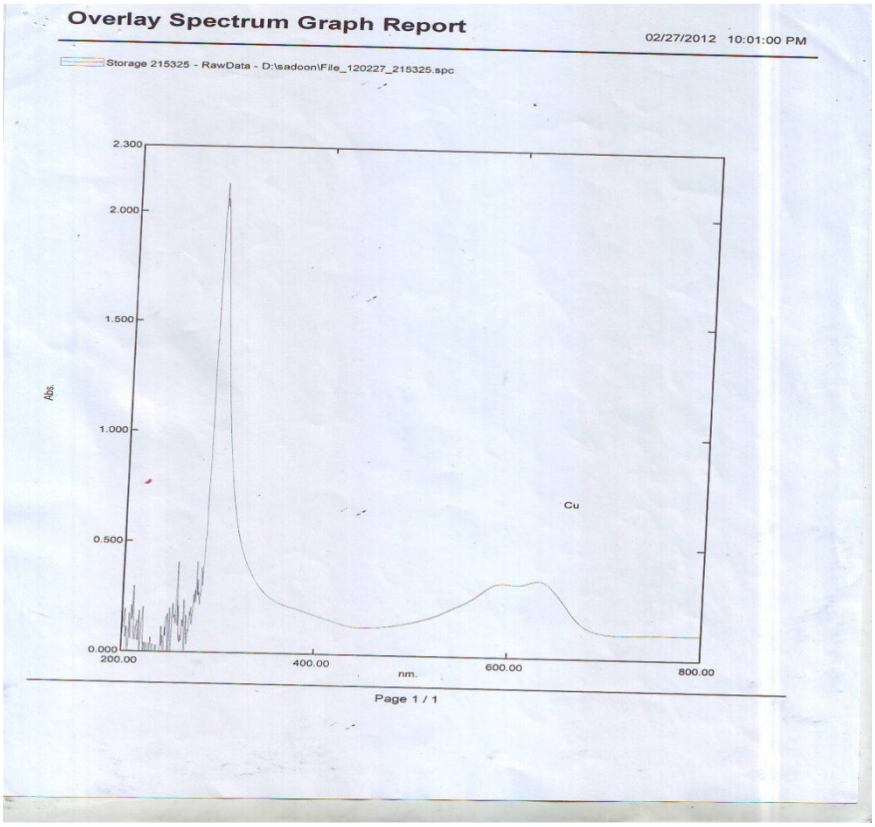


Figure (4) electronic spectra of Cu – AB25 complex

Determination the Complexes Formula :

By using the continous variation method , the formula of each complex was determined : (1:1) M:L formula for Ni- complex and Cu – complex , (1:2) M:L formula for Co – complex . Table (3) shows the molecular formula of these complexes .

Elements Analysis :

Elements analysis had completed for the ligand and the prepared complexes , table (3) shows the results of the element analysis .

Table (3) element analtsis data of the ligand and the complexes :

Com.	**AB25**	**Ni-AB25**	**Co-AB25**	**Cu-AB25**
M.F.	$C_{20}H_{13}N_2O_5SNa$	$NiC_{20}H_{17}N_2O_7S$	$CoC_{40}H_{26}N_4O_{10}S_2$	$CuC_{20}H_{17}N_2O_7S$
C	57.64 (55.90)	49.20 (48.57)	56.80 (55.10)	48.70 (47.32)
H	3.12 (3.00)	3.48 (3.10)	3.08 (2.82)	3.45 (3.01)
N	6.72 (6.64)	5.74 (5.21)	6.63 (6.01)	5.68 (5.12)
O	19.21 (18.90)	22.95 (22.31)	18.93 (18.23)	22.73 (22.01)
S	7.68 (6.99)	6.56 (6.11)	7.57 (6.88)	6.49 (5.51)
Na	5.52 (4.98)	----------	----------	----------
M	---------	12.03 (11.72)	6.97 (6.21)	12.89 (12.25)

Com. = compound
M.F. = molecular formula
M = metal

Molar Conductivity (Λ_m) Measurements :

The molar conductivity for the aqeous solutions of the ligand and the complexes (10^{-3} M) at 25°c were measured , the results shown in table (4) .

Determination the Complexes Magnatic Properties :

Magnatic properties of the complexes were measured due to Gouy Balance Methode . The effective magnatic momentum μ_{eff} at 25° c was calculated and the results are shown in table 4)(

Table (4) analytical and physical properties of the ligand and the complexes :

Compound	AB25	Ni-AB25	Co-AB25	Cu-AB25
M. W.	416.38	487.80	485.00	492.8
Λ_m(ms/cm^{-1})	3.721	4.15	0.182	4.08
)BM(μ_{eff}	----------	0.23	1.50	1.52
colour	Blue	Blue - green	=	=
Shape	----------	squar planar	tetrahedral	tetrahedral
hypridization	----------	Dsp^2	d^2sp^3	sp^3

IR Specra :

IR specra for the ligand and the complexes , in their solid state , were recorded in the range (400 – 4000) cm^{-1} with KBr discs . Figure (5 – 8) shows these spectra and the absorption bands of important groups of the ligand and its complexes are shown in table (5) .

Table (5) important IR absorption bands for ligand and the complexes :

Assignment	*AB25*	Ni-AB25	Co – AB25	Cu – AB25
N-H$_{(str.)}$	3435$_{(S)}$ 3300$_{(W)}$	3522$_{(S)}$ 3437$_{(W)}$	3446$_{(S)}$ 3335$_{(W)}$	3419$_{(S)}$ 2929$_{W)}$
C-H$_{(str.)}$	2924$_{(W)}$	3215$_{(W)}$	2950$_{(W)}$	2854$_{(W)}$
C=O$_{(str.)}$	1572$_{(S)}$	1624$_{(S)}$	1630$_{(S)}$	1624$_{(S)}$
C-N$_{(str.)}$	1234$_{(S)}$	1230$_{(S)}$	1300$_{(S)}$	1384$_{(S)}$ 1363$_{(S)}$
C=C$_{(str.)}$	1533$_{(M)}$	1530$_{(M)}$	1530$_{(M)}$	1506$_{(M)}$
S=O$_{(str.)}$	1024$_{(S)}$	1024$_{(S)}$	987$_{(S)}$	1109$_{(S)}$
S-O$_{(str.)}$	731$_{(S)}$	669$_{(S)}$	848$_{(S)}$	700$_{(S)}$
C-H$_{(ben.)}$	950$_{(M)}$	1815$_{M)}$	895$_{(M)}$	835$_{(M)}$
C-S$_{(str.)}$	632$_{(S)}$	632$_{(S)}$	630$_{(S)}$	675$_{(S)}$

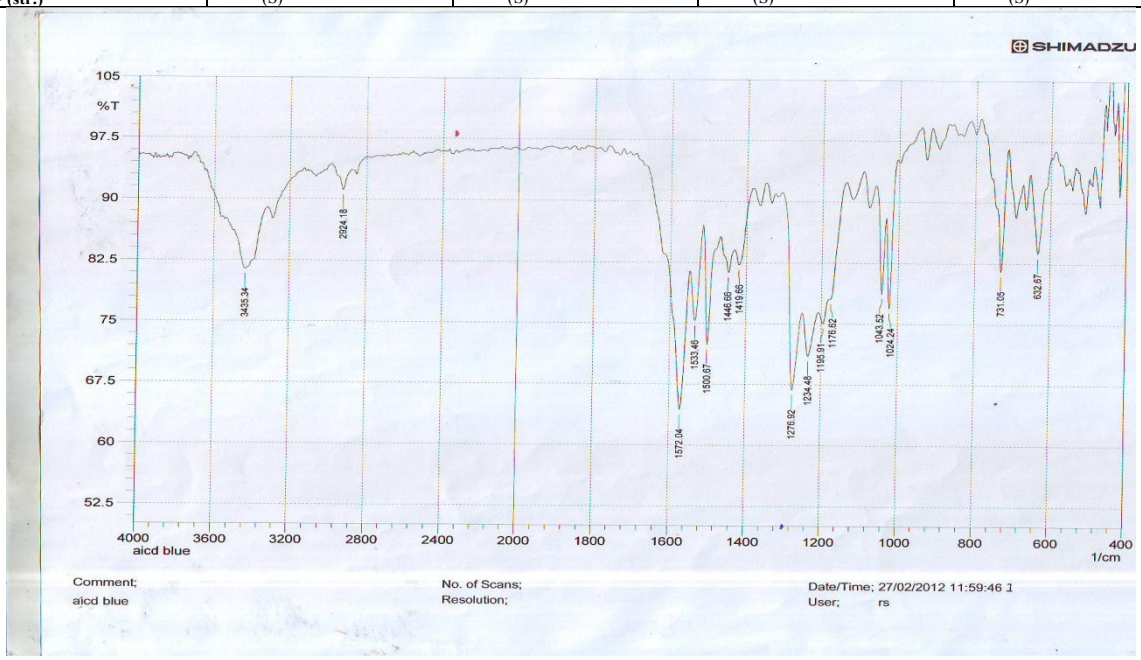


Figure (5) IR spectra of AB25 ligand

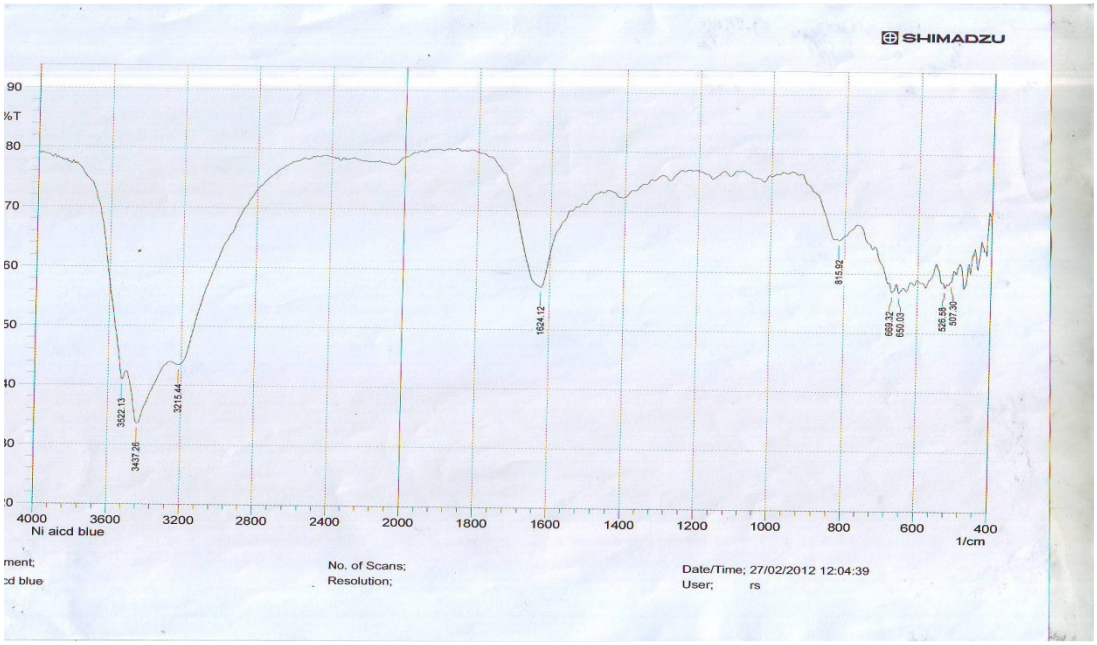


Figure (6) IR spectra of Ni- AB25 complex

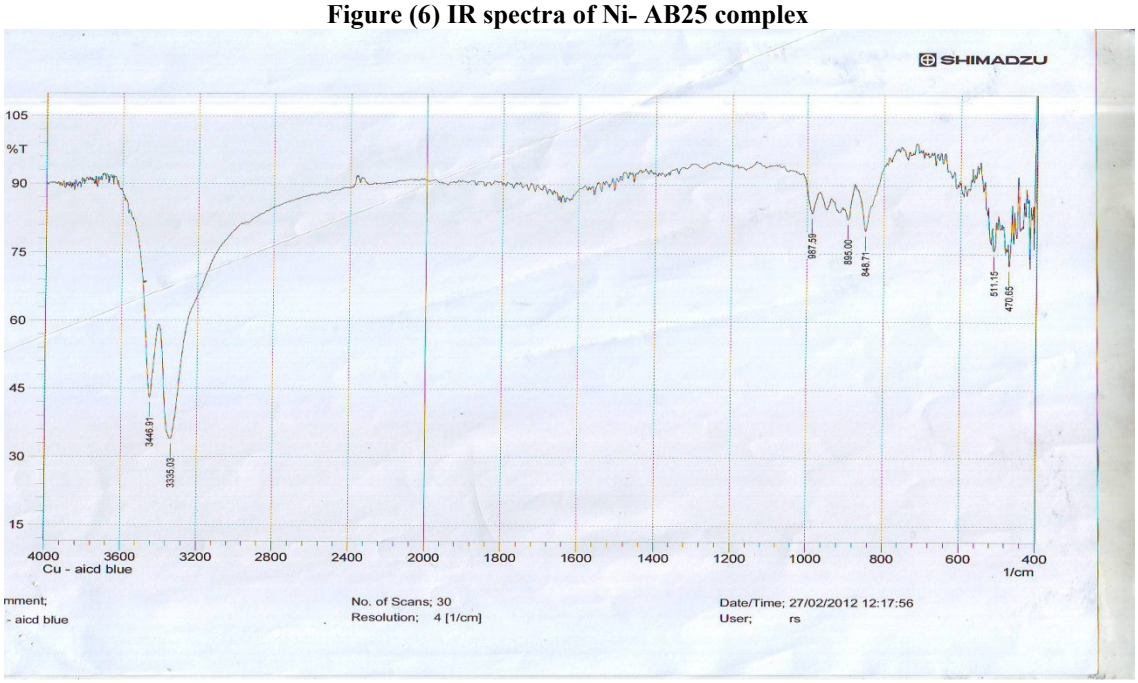


Figure (7) IR spectra of Cu- AB25 complex

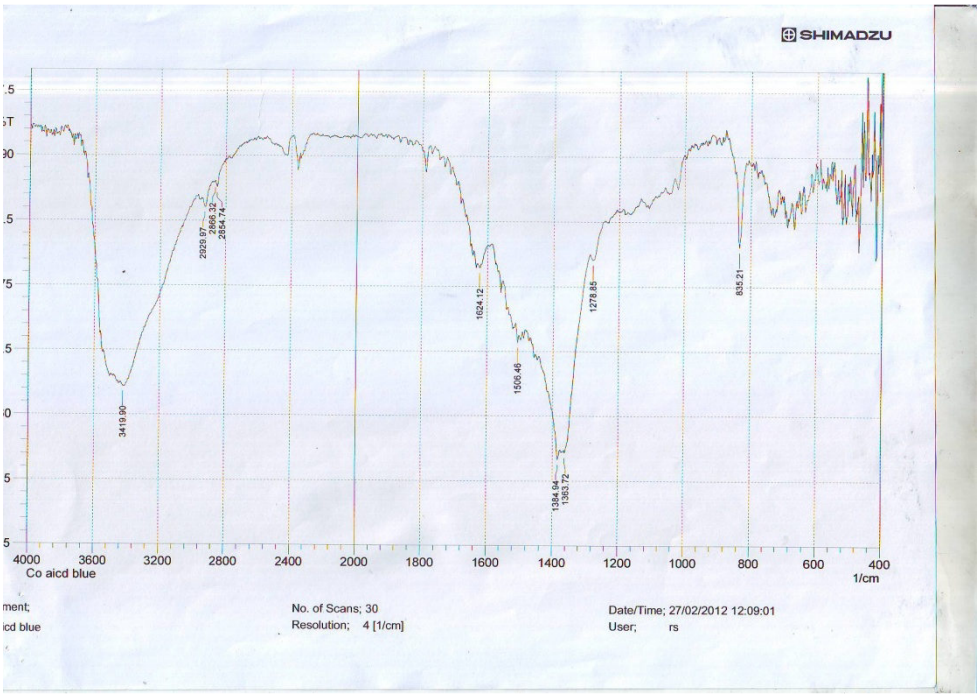


Figure (8) IR spectra of Co- AB25 complex

3 - Results and Disscusion

The most important IR absorption bands , in the ligand IR spectrum and the complexes IR specra within the range (4000 – 400) cm^{-1} , are shown in table (5) . The important stretching bands in the ligand IR spectrum belongs to N-H , C-H , C=O , C-N , S=O , S-O and C-S bands . The shifting observed in the IR sprctrum bands of the complexes supports that the coordination between the metals and the ligand via the NH , CO , SO3 groups and that lead to expect that the electronic environment of the metal atoms had been changed after the coordination process and complexes formation .

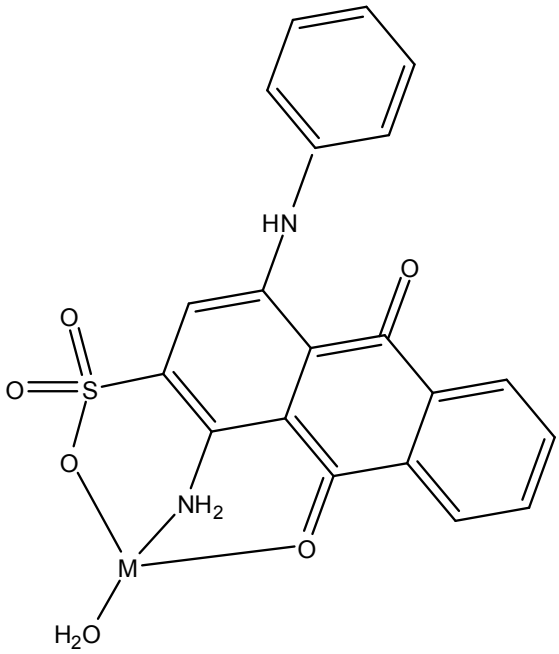
The ligand electronic spectrum shows that there are three principle bands ; 280 nm and 390 nm represent the position transitions of the aromatic rings while the third , 590 nm , belong to charge transfer band . This conclution agree with the reference (Chang 1975) . Clear displacement (50 nm) had occurred to these bands after the formation of the complexes , that refer to that the electronic environment of coordinated atom had been differed after the coordination process . This result agree with the published research which used like this ligand (Mohamd *et al.* 1984) .

The results of the molar conductivity measurements indicate that the ligand , Ni – complex and Cu – complex have good conductivity due to the positive charge on the coordination core and the nrgative charge on the neighbouring ion , whereas Co – complex has no conductivity due to the neutral coordination core .

The magnetic properties indicate that Ni – complex has diamagnetic properties , whereas Cu – complex and Co – complex have paramagnetic properties .

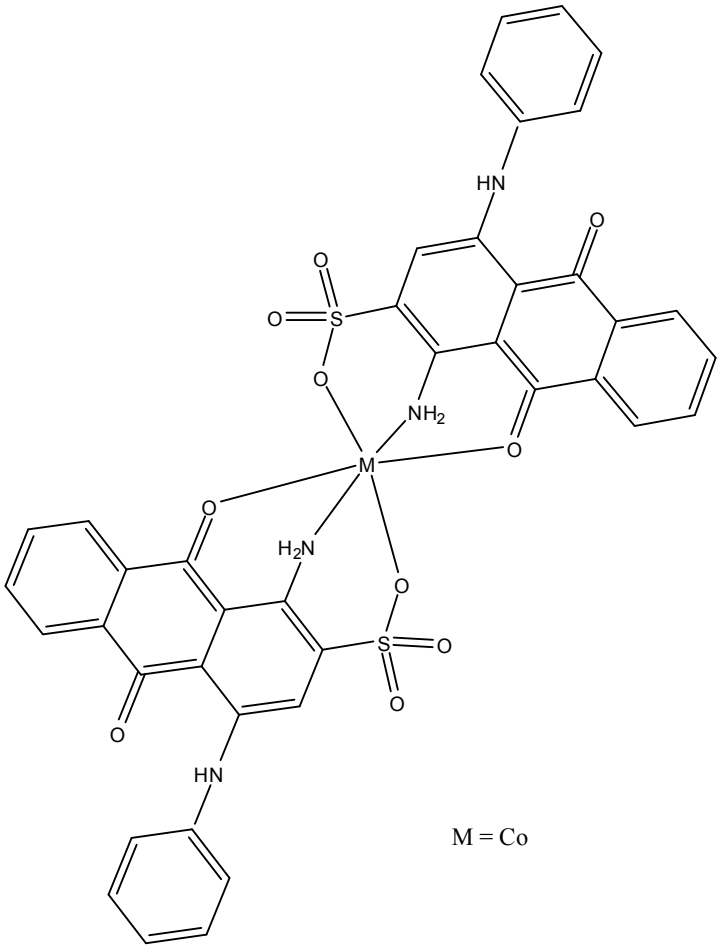
The suggested geometrical shapes of the complexes were squar planare for Ni complex and tetrahedral for Cu complex, whereas Co complex was octahedral . The figures (9 – 10) shows these shapes .

Acknowledgment : I thank all the teaching staff in chemistry department who help me to established this research . this work was supported by the University of Babylon ,Hilla , Iraq .



M = Ni or Cu

Figure (9) geometrical shapes of Ni and Co complexes



M = Co

Figure (10) geometrical shape of Co complex

4 – References

Joseph A. Loo and Peifeng Hu , J. Am. Soc. Mass Spectrum , 5 , 959 – 965 (1994) .
Hideyo Sindo and Theodor L. Brown , Journal of American Chemical Society , 87:9 , May 5 (1965) .
S. Malathy Sony , K. Saraboji , M.N. Ponnuswamy , J. Manonmani , M. Kandasmy and H.K. Fun , Cryst. Res. Technol. , 39 , No. 2 , 185 – 192 (2004) .
G. Wn , G. Wang , X. Fu and L. Zhu , Molecules , 8 , 287 – 296 (2003) .
L. J. Rashan , T. A. K. AL – Allaf , W. F. Halaseh and R. F. I. Khuzaie , Biologia Bratislava , 35 , 349 (1990) .
Sadik , A. Omowunmi and Hangwa , V. S. Patent : 6 , 602 , 989 , Appl. No. : 573993 (2003) .
H. A. Salih and G. H. Sheriff , Iraqi J. of Chem. , 15 , 68(1990) .
Robert R. Crichton , Biological Inorganic Chemistry An Introduction , Elsevier B. V. (2008) .
Jasem M. A. AL – Husain , J. of Babylon University /Pure and Applide Sciences / No. (2) / Vol. (20) : (2012) .
Jaafer A. Al – Rasaq , Coordination Chemistry , Baghdad University , Scinece College (1984) .
Al – Zamilly O. M. Yasser , Practical Biochemistry , Babylon University , Science College (2004) .
Lehninger Albert L. , Biochemistry , Worth Publishers Inc. New York (1975) .
Al – Kabsha T. S. and Asos A. S. , Physical Analytical Chemistry , Mousel University (1988) .
Al – Flaih K. Ahmad , An Introduction of Biochemistry , University of Mousel (1986) .
Zora M. Grahovac , Snezana S. M. , Emilija T. P. and Snezana B. Tosic , J. Serb. Chem. Soc. , 71 , 189 (2006) .
Pretsch P. Buhlmann and C. Affolter , Structure Determination of Organic Compounds , Sprenger – Verlag Berlin Heidelberg New York (2000) .
R. Chang , Physical Chemistry , University Science Books (1975) .
M. R. Mohamad , A. M. Hammon and S. A. Ibrahim , Z. Phys. Chem. , 265 , 203 (1984) .