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Synthesis and characterization of N-(4- Nitro benzylidene)-N-{2-[(4-nitrobenzylidene)-amino]-ethyl}-ethan-1,2-diamine as aligand and their metal complexes with Cobalt(II) , Nickel (II) & Cupper (II)

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Abstract:

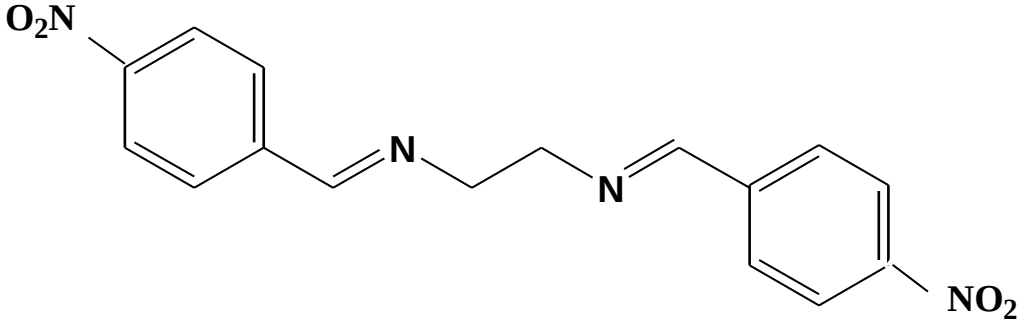
New chelate complexes of Co (II) , Ni (II) and Cu (II) with N-(4- Nitro benzylidene)-N-{2-[(4-nitrobenzylidene)-amino]-ethyl}-ethan-1,2-diamine were prepared.
All these chelate complexes have been characterized by (FT.IR) , (Uv – vis.) spectra , magnetic moment and conductivity measurements .
The studies suggested that the geometry around Co(II) and Cu(II) are tetrahedral shape and the geometry square planar shape is suggested to Ni(II) complex.

الخلاصة :

تم تحضير المعقدات المخلبية الجديدة لايونات الكوبلت(II) النيكل(II) و النحاس (II) مع الليكند N (4 - نايترو بنزليدين) - N - { 2 – [(4- نايترو بنزليدين) - امينو] أثيل } ايثان – 2,1 – ثنائي امين وقد تم تشخيص هذه المعقدات المخلبية بواسطة أطياف الأشعة تحت الحمراء (FT.IR) وأطياف الأشعة فوق البنفسجية والمرئية (U.V.- Vis.) وقياس العزم المغناطيسي وقياسات التوصيلية الكهربائية ثم أقترح الشكل رباعي السطوح لمعقدي الكوبلت (II) والنحاس (II) ، بينما أقترح الشكل المربع المستوي لمعقدالنيكل (II) .

Introduction:

As part of a study of the super molecular structures of compounds containing nitro groups, the structures of the title compounds were determined . The structure of N, Ń - bis (4- nitrobenzylidene) ethan – 1,2 – diamine [I] , has been reported very recently and it is clear that the determination reported have refers to the same phase as that in the previous report [(1)] Scheme (I) .



Scheme(1)

Metal complexes of Schiff bases are extensively studied due to synthetic flexibility , selectivity and sensitivity towards a variety of metal ions[2] .
They are found useful in catalysis , in medicine as antibiotic and anti inflammatory agents and in the industry as anticorrosion [3-9] .

Experimental:

A) Chemicals :

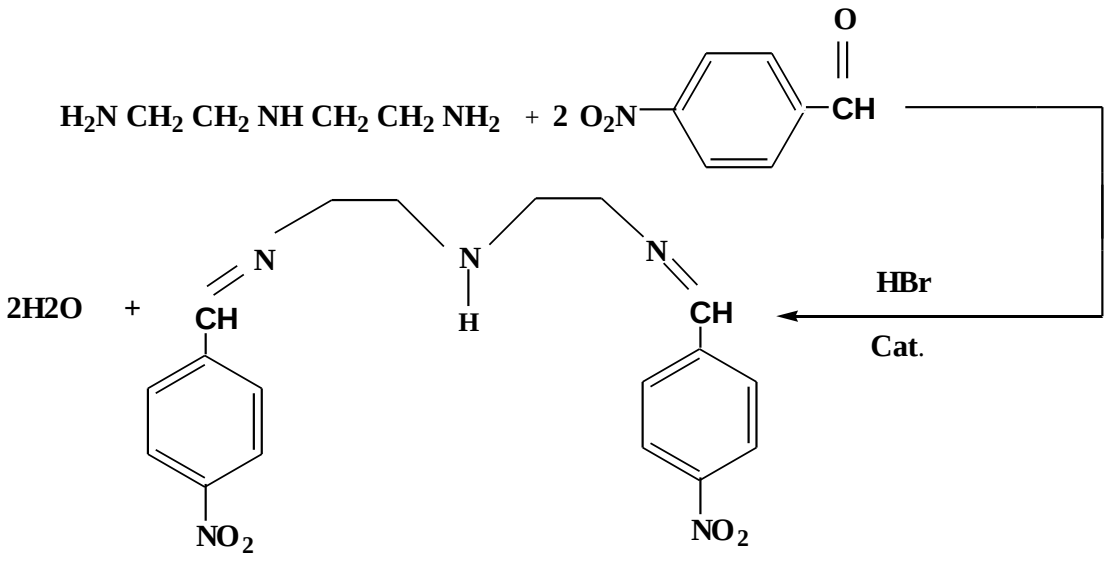
All chemicals used of reagent are grade .
In the preparation of metal chelates of Co (II) , Ni (II) and Cu (II) , $CoCl_2 .6H_2O$, $NiCl_2 . 6H_2O$, $CuCl_2 . 2H_2O$ were used for chelation from Flucka and Sigma companies .

B) Instruments :

FT.IR spectra were recorded on FT.IR – 8400S Shimadzu in the range (4000 – 400) cm^{-1} at Kerbala University . U.V. – Vis. Spectra of prepared compounds were done by U.V. – 1800 Shimadzu U.V. spectro photometer , conductivity measurements were obtained using WTW – digital meter at Kerbala University .

C) Synthesis of the Ligand:

Diethylene triamine (0.103g , 1mmol) was dissolved in (20 ml) ethanol and the mixture was refluxed with p – Nitrobenzaldehyde (0.302 g , 2 mmol) for (6hours),2drops of HBr were add as catalyst.
A pale – yellow precipitate was formed , the product was filtered off , recrystallized form , ethanol extracted by vacuum and dried over CaCl2 scheme (2) .



Ligand

Scheme (2)

D) Synthesis of Complexes :

The complexes were prepared by dissolving (0.738g, 0.5mmol) of ligand in 20ml of ethanol which then added dropwise with stirring to (1.0mmol)of MCL2 salts [M= Co(II) as CoCl2.6H2O (0.2379gm), Ni(II) as NiCl2.6H2O (0.2376gm), Cu(II) as CuCl2.2H2O (0.1705gm)] which dissolved in 25ml hot distilled water , the result mixture was allowed to reflux for (2hours) . The resultirs solution was left at room temperature for 30 min. The solid complex formed was filtered, washed thoroughly with ethanol and dried in vacuo over CaCl2.

E) Physical measurements :

Some physical properties are summarized in table (1) The data from complexes correspond well with the general formula ML2, where M = Cu(II), Ni(II) and Co(II) ; L= C18H19N5O4 :

Table (1) : Physical properties of the prepared Ligand and its complexes

Compound symbol	Formula	M.P. (C^O)	Color	Yield %	Meff B.M.	Λ $\Omega^{-1}.mol^{-1}.m^2$
L	$C_{18}H_{19}N_5O_4$	173-175	Pale yellow	70	-	-
C_1	$[Ni\ (C_{18}H_{19}N_5O_4)_2]\ Cl_2$	182-184	Greend blue	80	0	35.
C_2	$[Cu\ (C_{18}H_{19}N_5O_4)\ Cl_2]$	198-190	Pale green	75	1.4	0
C_3	$[(Co)_2(C_{18}H_{19}N_5O_4)_4\ Cl_2]Cl_2$	208-210	Brown	70	3.9	16

Inferared Spectra of the ligand and its complexes:

Selected FT-IR absorption of ligand and its complexes are given in table (2) . In order to study the binding of the ligand to metal in the new complexes , the IR spectrum of the free ligand was compared with the spectra of the metal complexes .

The medium band is observed at (3487 cm-1 - 3558 cm-1) in the infrared spectra of the free ligand which is characteristic of the υ (NH)(10), In the spectra of all the new complexes, this band is shifted to the region at (3315 cm-1 - 3497 cm-1) .
The strong band is observed at (1633cm-1)in the spectrum of free ligand which is characteristic of the azomethine group υ (C=N)(11). If the ligand coordinate through the nitrogen atom, it is expected that there must be a reduction in the azomethine frequency due to the lowering of electron density upon coordination. In the spectra of all the new complexes, this band is shifted to the region (1602 cm-1 - 1612 cm-1) indicating the coordination of the Schiff bases through nitrogen atom(12).
New bands in the region (530 cm -1) and (509 cm -1) were observed in the spectra of metal complexes . These bands were not present in the spectra of free ligand, and they due to υ(Ni - N) , (Cu - N) and (Co - N) stretching respectively (13), figures (1,2,3&4).
The infrared spectra data lead to suggest that ligand behaves as a bidentate chealating agents , and the coordination sites through nitrogen atoms for two azomethine groups , to form six membered ring which is kinetically stable .

Table (2):- FT.IR. bands of ligand and it's complexes (KBr disk , cm^{-1})

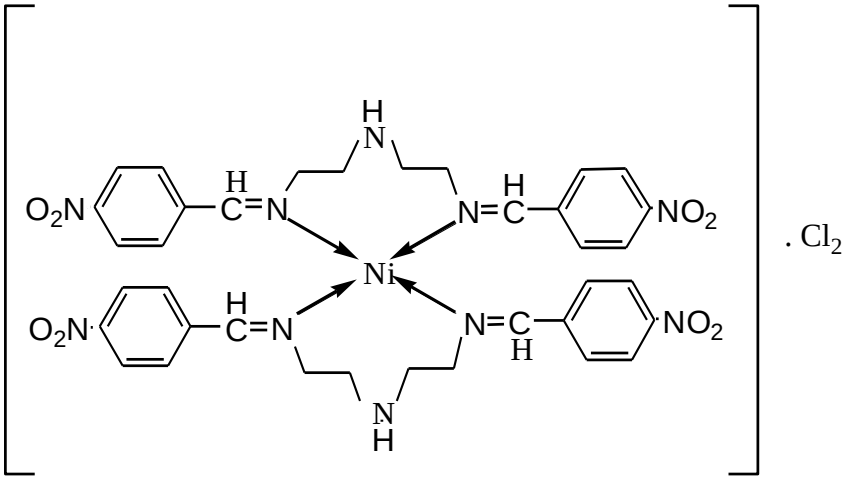
groups	Ligand	Ni - L	Cu – L	Co – L
υ (N- H)	3487 – 3558	3315 - 3341	3419	3429
υ (C= N)	1633	1602	1612	1602
Δ(N- H)	1495	1485	1460	1462
υ (C- H)	3082 – 3140 (956)	2930	2930	3117
υ (C – N)	1244	1196	1086	1098
υ (-No_2)	1358	1365	1372	1354
υ (M- N)	-	530	530	509

Electronic Spectra:

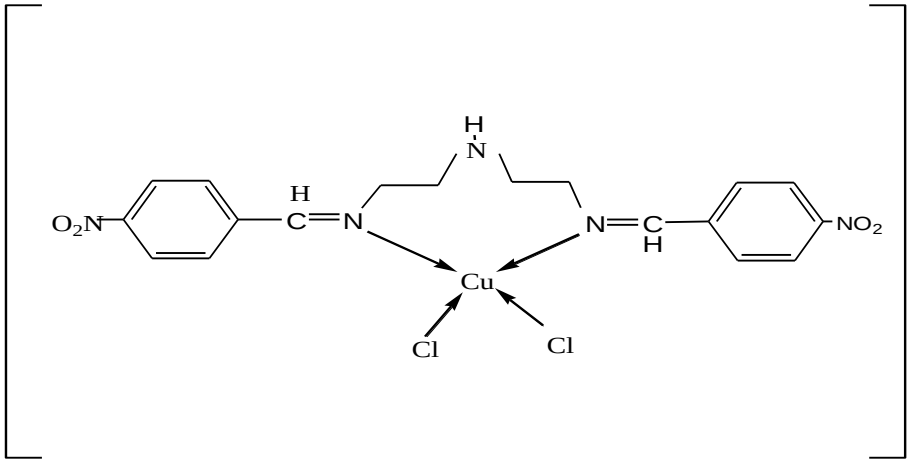
The spectral data of prepared complexes are listed in table (3).
The electronic spectra of Co(II)complex shows absorption band at (16447 cm-1) , this is assigned to 4A2g → 4T2g (F) transition . corresponding with previous studied of tetrahedral complexes(14) , the Ni (II) complex show band at (16474 cm-1) , which was suggesting the existence of 1A1g → 1B1g transition . which is characteristic of square planar stereo chemistry (15) . while the Cu (II) complex show band at 23201 cm-1 , which may assigned to 2Eg →2T2g transition , suggesting a tetrahedral structure (16) .
The electronic spectra of Co (II) , Ni (II) and Cu (II) complexes are appeared intense bands at(33670 cm-1, 33112cm-1 and 30211cm-1) respectively , these peaks are assist to charge transfer . Figures (5,6,7&) .
The (metal : ligand) ratios of complexes were determined by molar ratio method . The ratio of metal ion to ligand molecules was (2:1)

Table (3):- Electronic spectra of ligand and their complexes

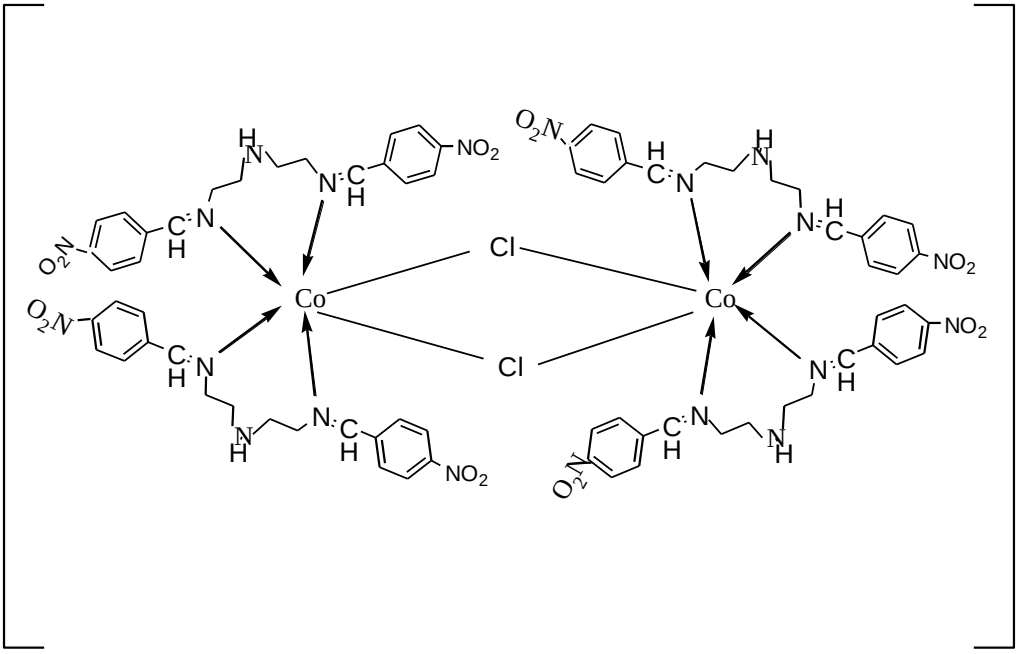
Comp.	Abs. bands (cm^{-1})	Transitions type	Magmetic Moment B.M.	Shape of complexes
[Ni ($C_{18}H_{19}N_5O_4$)$_2$ Cl_2]	16474 33112	C.T. $^1A_1g \rightarrow {}^1B_1g$	0.0	Square planar
[Cu ($C_{18}H_{19}N_5O_4$)$_1$ Cl_2]	30211 23201	C.T. $^2Eg \rightarrow {}^2T_2g$	1.4	tetrahedral
[Co ($C_{18}H_{19}N_5O_4$)$_2$ Cl_2]	16447 33670	C.T. $^4A_2g \rightarrow {}^4T_2g$	3.9	tetrahedral



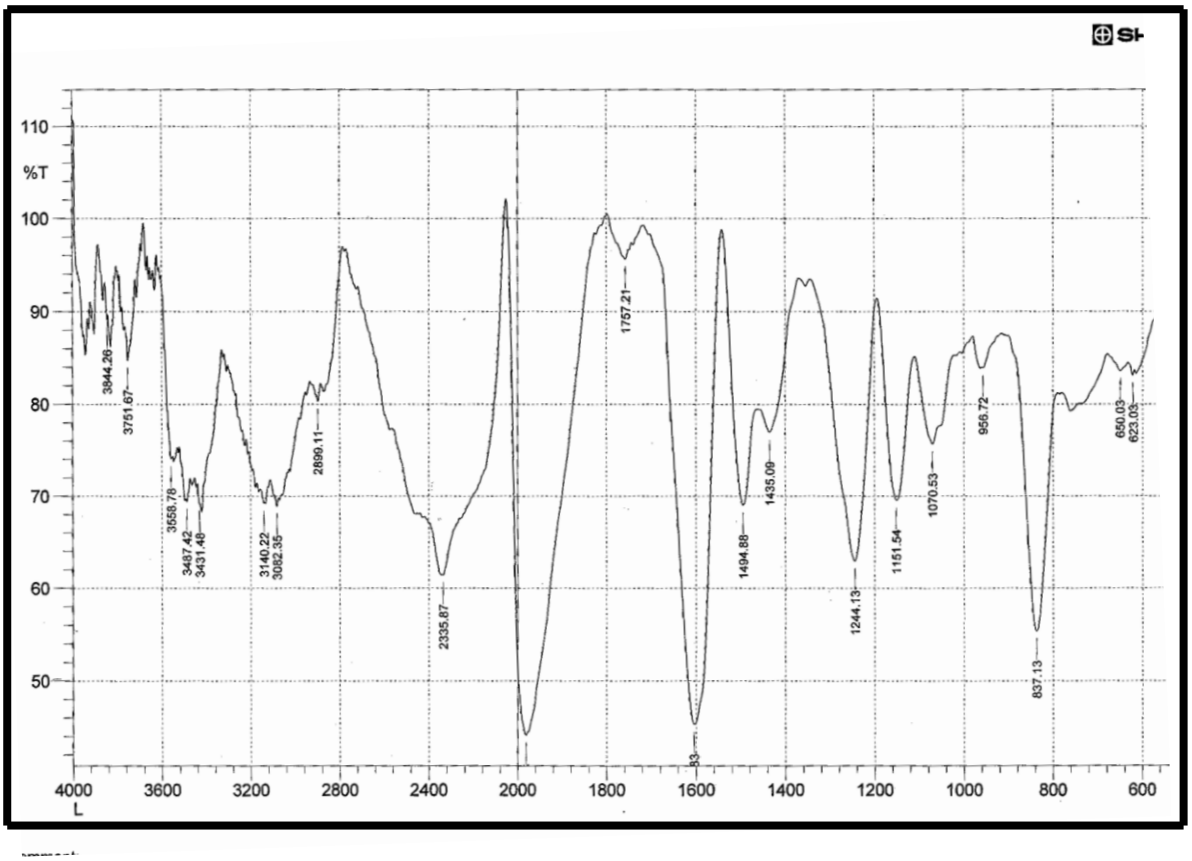
Scheme (3): C_1 Complex



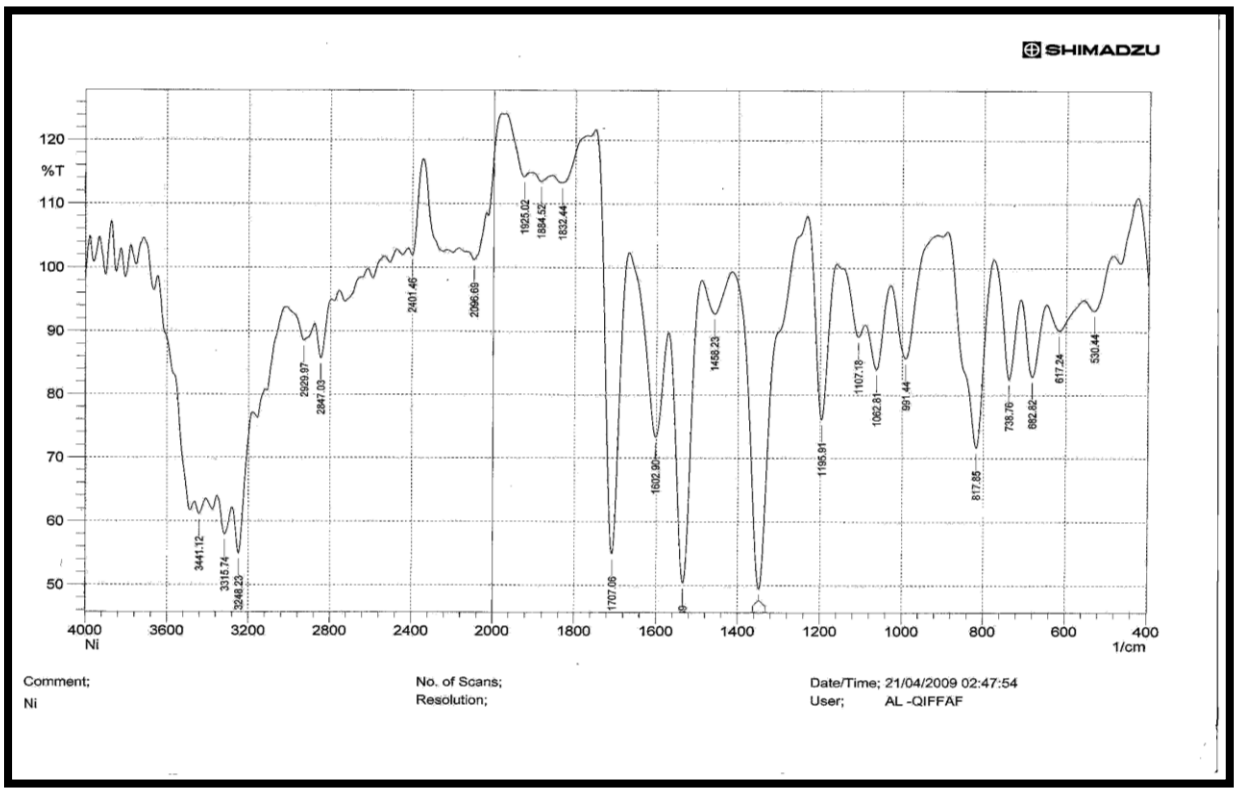
Scheme (4): C_2 Complex



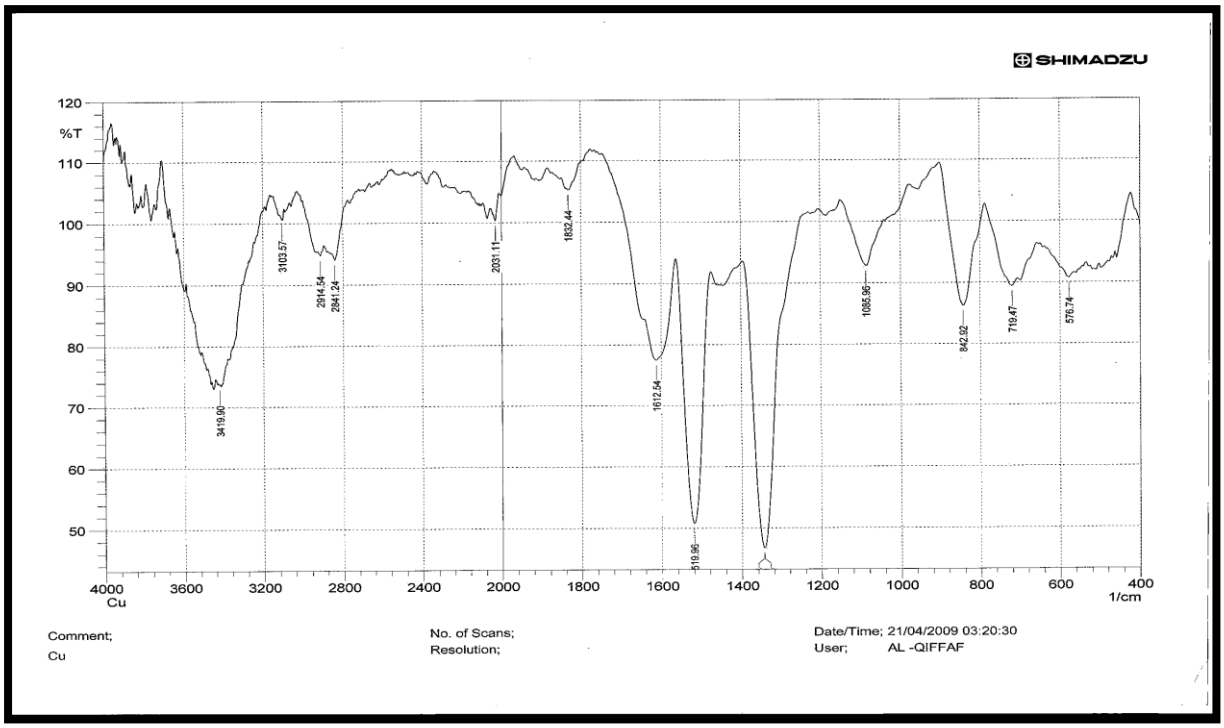
Scheme (5): C_3 Complex



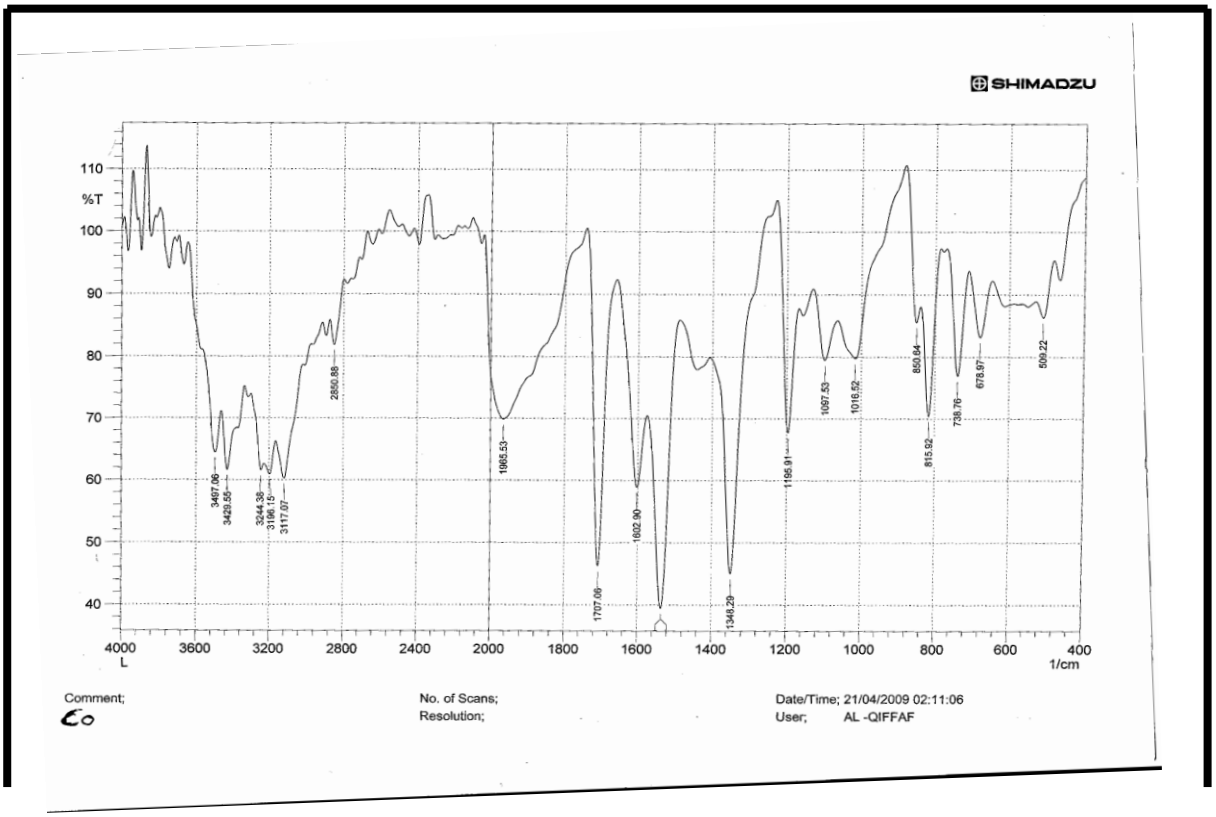
Figure(1): FT.IR . spectrum of ligand



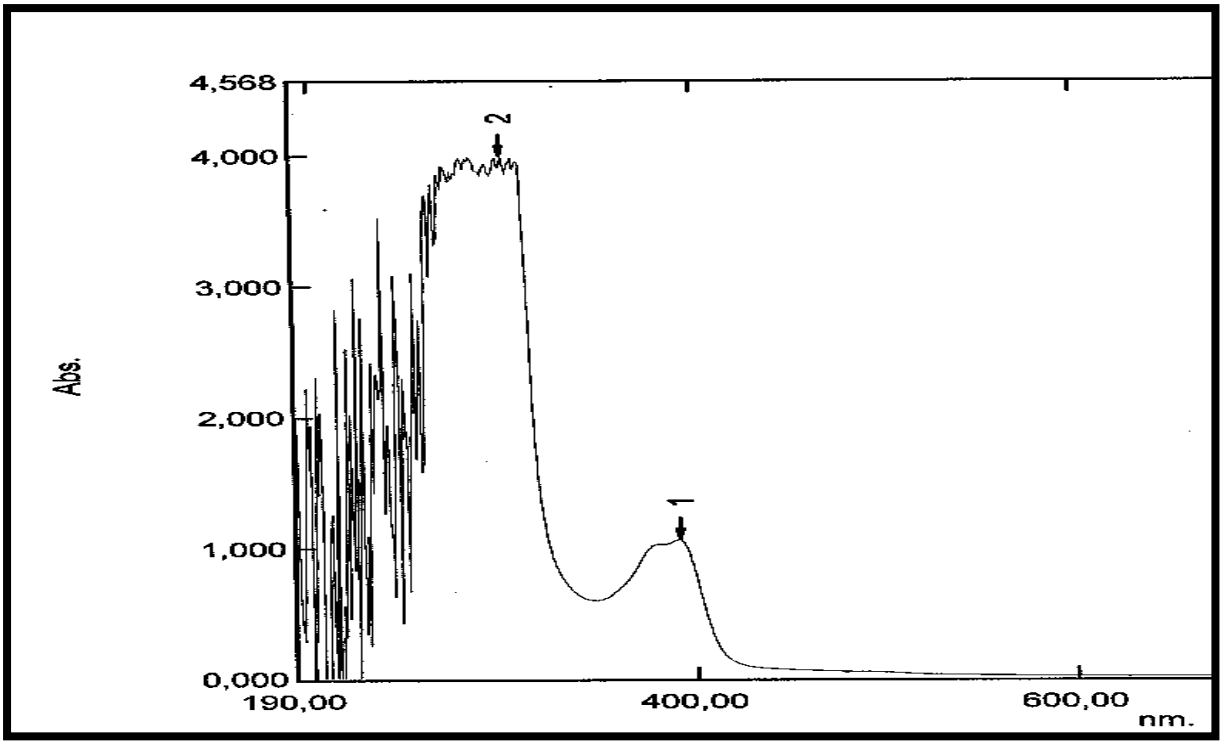
Figure(2): FT.IR spectrum of (C_1) complex



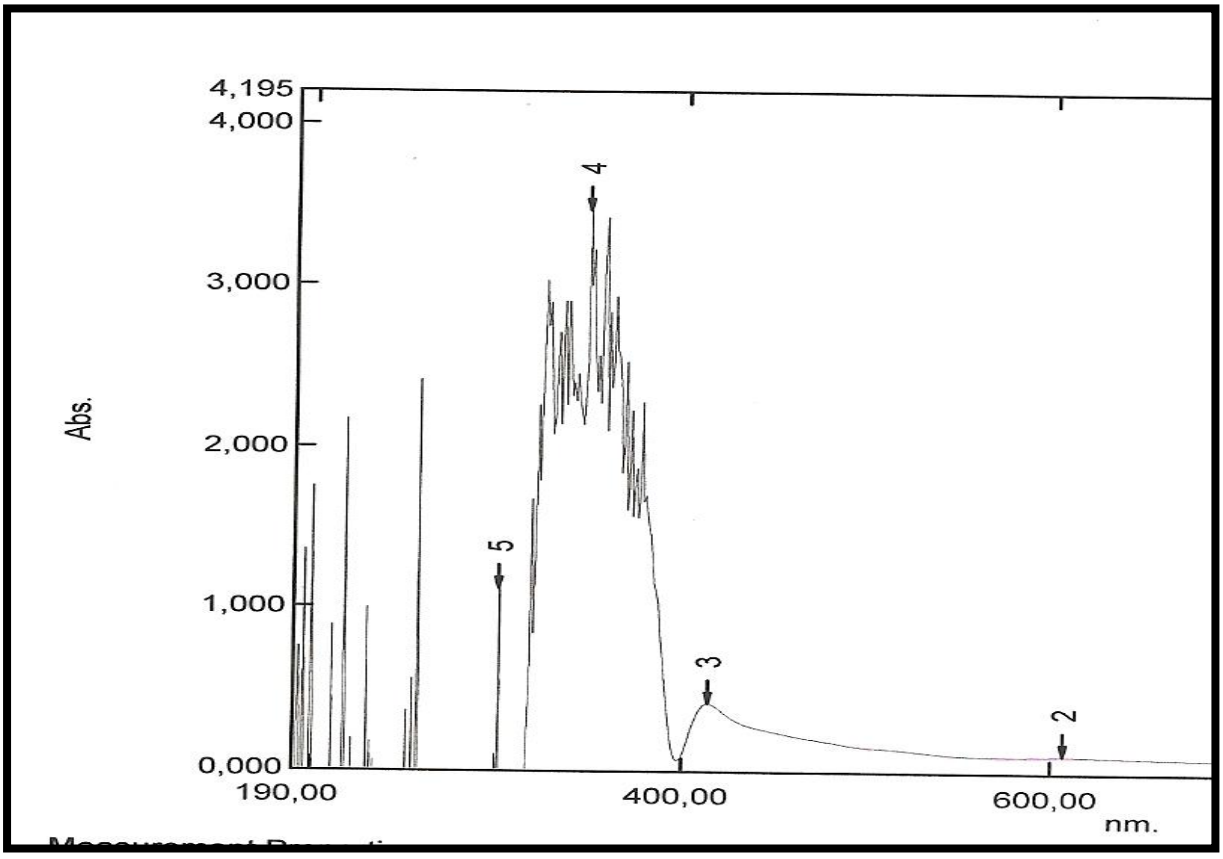
Figure(3): FT.IR. spectrum of (C_2) complex



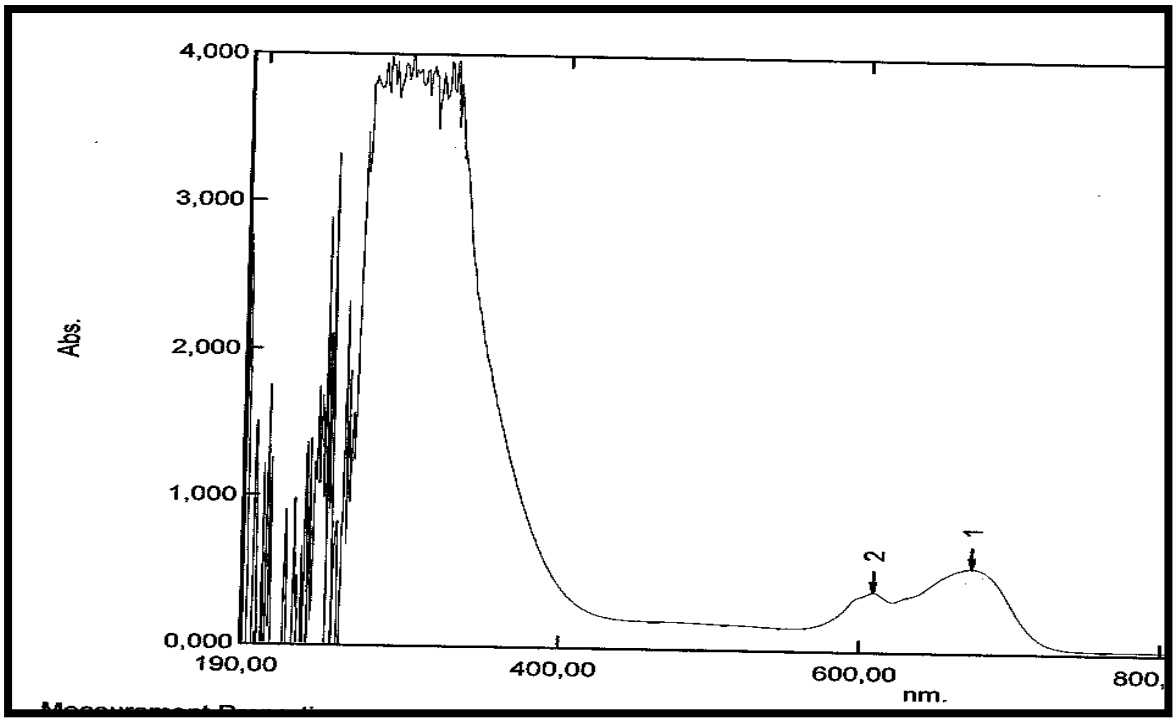
Figure(4): FT.IR. spectrum of (C_3)complex



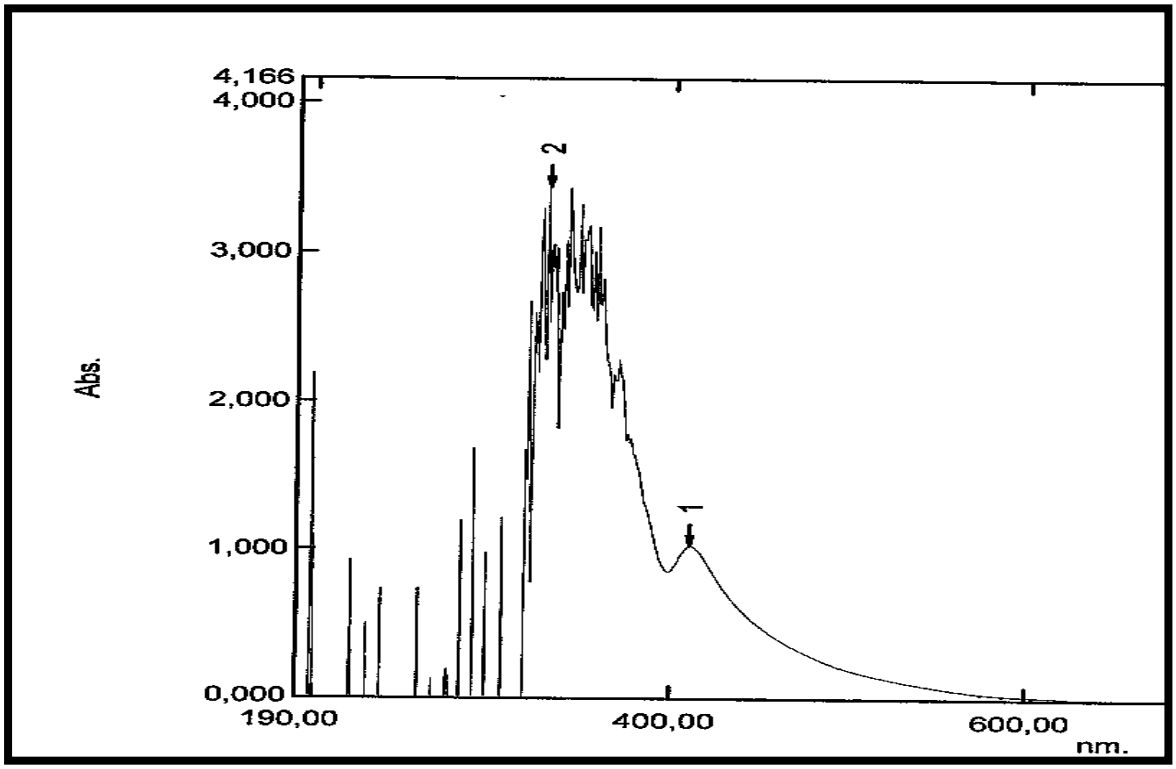
Figure(5): Electronic spectrum of ligand



Figure(6): Electronic spectrum of (C_1) complex



Figure(7): Electronic spectrum of (C_2) complex



Figure(8): Electronic spectrum of (C3) complex

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