تحضير وتشخيص معقدات فلزية جديدة لألفا أمينونتريل مشتقة من بارا ميثوكسي بنزالديهايد مع الأمينات الأروماتية

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الخلاصة

حضرت معقدات فلزية جديدة لبعض أيونات العناصر الانتقالية [Cu(II), Ni(II),Co(II), Fe(III)] مع الليكاندين المحضرين سابقاً HL_I = (بارا–مثيل انيلينو)– بارا ميثوكسي فنيل اسيتونتريل و HL_{II} (بارا ـ ميثوكسي أنيلينو) –بارا ميثوكسي فنيل اسيتو نتريل . حضر الليكاندان بطريقة ستريكر بمفاعلة بارا– ميثوكسي بنزالديهايد مع بارا – تولودين وبارا – أنسيدين على التوالي. شخصت تراكيب المعقدات الفلزية الجديدة بوساطة الامتصاص الذري اللهبي فضلا عن أطياف الأشعة تحت الحمراء والأشعة فوق البنفسجية– المرئية. حددت ايضا الخصائص المغناطيسية والتوصيلية الكهربائية في مذيب DMF للمعقدات الفلزية، كان سلوك الليكاندات ثنائية السن يرتبطان بالأيونات الفلزية عن طريق ذرتي النتروجين لمجموعة الفا–امينو ومجموعة النتريل عدا المعقد C_6 سلك الليكاند HL_{II} سلوكا احادي السن بارتباطه مع أيون Ni(II) عن طريق مجموعة النتريل فقط .

Synthesis and Characterization of New Metal Complexes of α-Aminonitriles Derived from P- Methoxybenzaldehyde with Aromatic Amines

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Abstract

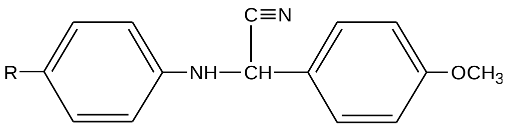
New metal complexes of some transition metal ions [Fe(III) , Co(II) , Ni(II) and Cu(II)] of two previously prepared ligands HL_I=(P-methyl anilino)- P-methoxy phenyl acetonitrile and HL_{II} =(P-methoxy anilino)-P- methoxy phenyl acetonitrile were synthesized. The two ligands were prepared by Strecker's procedure which included the reaction of P-methoxybenzaldehyde with p-toluidine and P-anisidine respectively. The structures of the new metal complexes were characterized by atomic absorption , i.r and U.V.-visible spectra . Magnetic susceptibilities and conductivity measurements in DMF of metal complexes were also studied. These ligands coordinate as abidentate molecules through nitrogen atoms of α-amino group and nitrile group except the complex C_6 of the ligand HL_{II} coordinates as monodentate with Ni(II) ion through nitrile group only.

Introduction

The chemistry of nitrile and α-aminonitrile compounds and their derivatives has received special attention because of their application as potential ligands for a large number of metal ions (1-5).

Strecker was the first to prepare α-amino nitriles for treating aldehydes or ketones by their treatment of alkaline cyanide and salts of amines (6). The ligands (HL_I and HL_{II}) previously prepared were synthesized by a modified Strecker's procedure (7).

Nitriles and α-aminonitrile derivatives had a biological activities (8,9) as herbicides (10) , pharmacological agents (11) and biological synthesis of chemical compounds by it's microbial metabolism in some organisms (12). Complexes containing more than ametal centre represent the synthetic models of ferromagnetic interaction between the metal centers which can explain oxidation- reduction processes in biological systems in addition to their catalytic and biological activities (13-16). Beside that, some aminonitriles were used to prepare racemic compounds (17) . In this work the synthesis and the characterization of new metal complexes of some transition metal ions [Fe(III), Co(II), Ni(II) and Cu(II)] of HL_I(P-methyl anilino)- P-methoxy phenyl aceto nitrile and HL_{II} (P-methoxy anilino) –p- methoxy phenyl aceto nitrile are studied . Coordination behaviour of ligands with metal ions were investigated The structural formula of two ligands are illustrated in scheme(1).



R= CH_3 in HL_I with M=Ni(II), Co(II) and Fe(III);
= OCH_3 in HL_{II} with M=Cu(II), Fe(III) and Ni(II).

Scheme(1):α-aminonitriles derived from P- methoxy benzaldehyde with aromatic amines.

Experimental

Apparatus

Melting points (uncorrected) were obtained by using Gallenkamp MF-600-010F melting point apparatus. Infrared spectra of metal complexes were recorded as CsI discs on Perkin-Elmer 1310R. Spectrophotometer. Electronic spectra of two ligands and their complexes in DMF were recorded on U.V.-visible spectrophotometer Shimadzu U.V.-160A. Electrical conductivities of metal complexes, in DMF (10^{-3}M) were measured at room temperature by using Hunts Capacitors Trade Mark (British) . Magnetic susceptibility (μ_{eff} B.M) of metal complexes were measured at room temperature by Faraday method using Balance, magnetic susceptibility, model MSB-Mk-1. Determination of metal content (%) of complexes were carried out by using Varian-AA775, Atomic Absorption spectrophotometer and Perkin-Elmer 5000 Atomic absorption spectrophotometer.

Materials and Methods

Metal salts Fe $(NO_3)_3$. $9H_2O$ 99.9%, $Co(NO_3)_2$. $6H_2O$ 99% (Fluka); $Ni(NO_3)_2$. $6H_2O$ 99.9%, $Cu(NO_3)_2.3H_2O$ 99% (Merck) ethanol absolute 99% (Fluka) were used as received from the suppliers. Dimethyl formamide (DMF) was dried and distilled prior to use (18) .

Preparation of α-aminonitriles (HL_I and HL_{II}) :

The aldehyde p-methoxy benzaldehyde 0.05 mole was dissolved in 50 ml of glacial acetic acid , (p-toludine , p-anisidine) sulfonic acid was added in small portions to bring the pH to 2 , followed by the additions of 0.05 mole of the amine. The pH was adjusted to 3-4 by adding concentrated H_2SO_4 drop wise . KSCN 0.05 mole was added to the mixture which was kept stirring . The end of the reaction was checked by the disappearance of the starting material (the amine) and development of a higher spot on T.L.C . The reaction mixture was poured on ice and made slightly alkaline with ammonia . The solid product was filtered , washed with water and dried .

Preparation of metal complexes of HL_I (C_1 of Ni(II) , C_2 of Co(II) and C_3 of Fe(III)) and HL_{II} (C_4 of Cu(II) , C_5 of Fe(III) and C_6 of Ni(II)):

A solution of a metal salt of Fe(III), Co(II), Ni(II) and Cu(II) in absolute ethanol was added to ethanolic solution of the ligand with a continuous stirring. The molar ratio of the reactants was 1:2 in C_1 , C_2 and C_6 , 1:1 in C_3 and 2:2 in C_4 and C_5. Precipitation of C_4 and C_5 took place immediately, while precipitation of other complexes required heating under reflux for 30-60min. The products were filtered off , washed several times with ethanol and dried under vacuum.

Results and Discussions

a) Physical data and atomic absorption :

Table (1) describes the physical properties of metal complexes of HL_I and HL_{II}. The suggested molecular formula were further supported by spectral studies. Atomic absorption of few complexes showed less agreeable results because of technical errors in the instrument. All the complexes were insoluble in water , methanol and ethanol .The complexes are however , soluble in DMF and chloroform.

b) Infrared spectra:

Important characteristic stretching frequencies of the ligands and their metal complexes are described in Table (2) and their spectra are shown in figure(1). The i.r spectrum of complexes C_2, C_3 and C_5 showed shifts in position of $\upsilon_{C\equiv N}$ band (19,20) this band is increased in complex C_3 and C_5 from free ligand. This refers to C≡N coordination to metal ion via-σ donation of the lone pair of electrons of nitrile nitrogen atom (19). The spectra of complex C_2 showed decreases of $\upsilon_{C\equiv N}$, the decreases were attributed to metal dπ to ligand Pπ^* back-bonding (1,2,20). In complexes C_1, C_4 and C_6 showed the bands of $\upsilon_{C\equiv N}$ splitting which refers to coordination of metal ion to nitrogen atom (2,20). The FTIR spectra of complexes C_1 and

C_2 exhibited the υ_{N-H} and δ_{N-H} (1500-1516)cm^{-1} shifted to lower frequencies from free ligand while those of compared with the C_3, C_4 and C_5 showed the disappearance of the υ_{N-H} and δ_{N-H} . These changes which refer to coordination of α-amino nitrogen to the metal ion (15,20). The complex C_6 exhibited achange of υ_{N-H} to ahigher frequency. This is attributed to the absence of both hydrogen bonding and coordination with Ni(II) ion (21). The bands appeared at (3321-2970) and (2960-2843) cm^{-1} were assigned to aromatic and aliphatic υ_{C-H} respectively (22). The bands related to aromatic $\upsilon_{C=C}$ vibration appeared at (1603-1612) cm^{-1} (23) . The bands related to υ_{C-O}, δ_{CH3}, and υ_{C-C} vibrations appeared at (1078-1015) , (1306-1466), (1182-1173) and (966-934)cm^{-1} respectively (22,23,24). Nitrate ions exhibited vibration modes related to ionic behaviours in complexes C_1,C_2, C_3,C_4 and C_6 , while bidentate bonding in C_3 and C_5 and monodentate in C_5 (21,23) . Vibration modes of lattice and coordinated water were observed in spectra of C_3, C_4, C_5 and C_6 (21,25). New bands appeared at lower frequencies were assigned to M-N≡C, M-N and M-O stretching modes (21,23,26). From the above spectra, it is concluded that the ligands HL_I and HL_{II} act as bidentate ligand coordinating through the nitrogen atoms of the α-amino group and the nitrile group, This is in the case of C_1, C_2, C_3, C_4, and C_5 complexes, but in the case of C_6 complex the ligand would coordinate through the nitrogen atom of nitrile group with Ni (II) ion.

C) Electronic spectra, Magnetic susceptibility and conductivity measurements:

The electronic spectra of the prepared α-aminonitrile showed main band observed in the u.v region and was assigned to $\pi\rightarrow\pi^*$ transition of the aromatic rings and C≡N group and other conjugated system (24). The spectrum of HL_{II} showed low intensity band observed at (27419)cm^{-1} was assigned to $n\rightarrow\pi^*$ transition may be masked by $\pi\rightarrow\pi^*$ band .Table (3) describes bands of maximum absorption of ligands and their metal complexes in DMF with their assignments together with crystal field parameters (Dq/B`, B` , 10Dq and β) . The latters were determined by applying band ratios on Tanabe Saugano diagrams of specified metal ion (27-29). The absorption bands of ligands and their metal complexes are shown in figure (2). Complexcation with metal ion caused shifts of ligand bands to lower wave numbers and the appearance of new bands in the visible and near i.r. regions. These additional bands may be related to M-L charge transfer bands and ligand field (d-d) transitions (27-29).

Ni (II) complexes C_1 and C_6:

The complex C_1 was found diamagnetic which refered to a square planar geometry (23,30). The spectrum of these complex in DMF showed two bands attributed to a square planar Ni(II) transitions (23,27,30,31). The spectrum of the complex C_6 exhibited two bands were attributed to octahedral Ni(II) complexes (27,28) . The band appeared at (27274)cm^{-1} was due to (C.T) transition (27-29). By applying band energies and ratio υ_2/υ_1 (1.44) on Tanabe Saugana diagram, the energy of 10Dq and υ_3 was calculated from diagram and the results are given in table (3) . The value of β indicated covalent character (28) . Magnetic moment of the complex C_6 was 3.78 B.M came in an agreement with those of octahedral geometry (15,23,25,27) .

Co (II) complex C_2:

Magnetic moments (μ_{eff} =3.81B.M) of Co(II) complex referred to a tetrahedral geometry (32). The spectrum of this complex in DMF exhibited a single band at (10256)cm^{-1} was assigned to (υ_2) and multiplet of three bands appeared at (15000, 17046 and 19231)cm^{-1} and the average value of muliplet (17092)cm^{-1} was assigned to (υ_3). The position of the absent band (υ_1) was calculated by applying band ratios and energies of absorptions band on Tanabe Saugano diagrams (27-29). The transitions of these bands are given in table (3) of tetrahedral Co(II) geometry (27-29) the value of β indicates a covalent character (27,28) . Band observed in complex was referred mainly to ligand →metal charge transfer (28).

Fe (III) complexes C_3 and C_5:

Magnetic moments of C_3 and C_5 were 5.57 and 3.89BM respectively. Magnetic moment of C_5 is lower expected due to the presence of antiferromagnetic interaction of the dimeric octahedral Fe(III) complexes (16,25,28). Low intensity bands were observed in the spectra of the two complexes were attributed to the forbidden transition which was the characteristic of d^5 octahedral complexes (27-29). The band at (23077) cm^{-1} in C_3 was assigned to L→M(C.T) transition (27-29).

Cu (II) complex C_4:

Magnetic moments of the complex C_4 (μ_{eff} =1.89 B.M) suggests that the unpaired spins of two copper atoms are coupled through conjugated ligand bridge. The spectra of the complex showed that three bands were attributed to spin allowed the transitions of Jahn Teller tetragonally distorted octahedral Cu(II) complexes (15,26-28) .

Conductivity measurements of complexes C_1, C_2, C_3,C_4, and C_6 in DMF (10^{-3}M) showed that they were electrolytes with ionic ratio of 1:2 in C_1 C_2, C_4 and C_6 and 1:1 in C_3 while C_5 was found to be non electrolytic (33).

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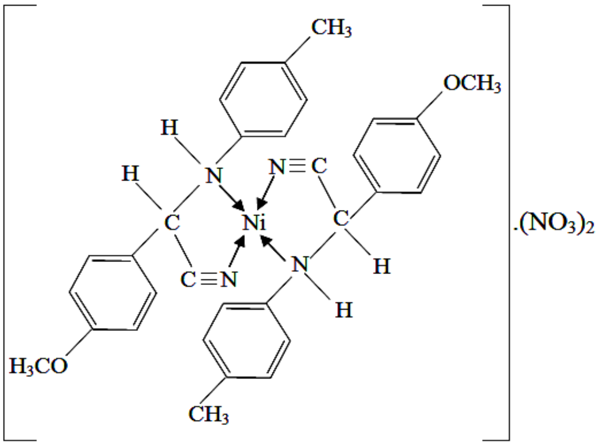
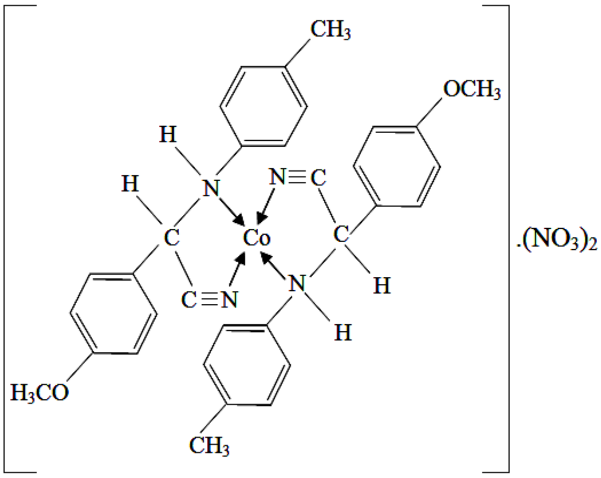
According to these observations and data obtaind from atomic absorption and i.r spectra the structures of complexes were suggested as illustrated .

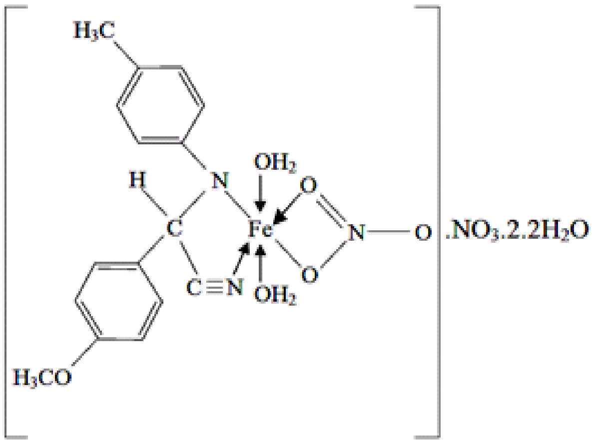
C$_1$: $[Ni(HL_I)_2].(NO_3)_2$



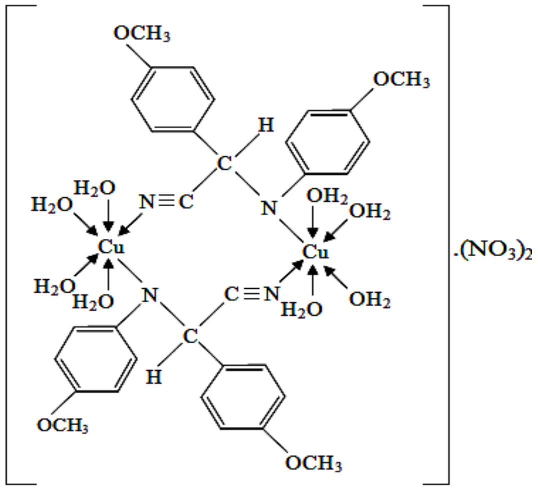
C$_2$: $[Co(HL_I)_2].(NO_3)_2$



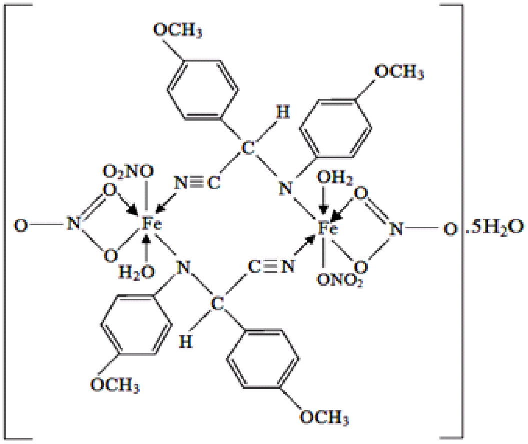
C3: $[FeL_INO_3(H_2O)_2].NO_3.2.2H_2O$



C4:



C5: $[Fe_2(L_{II})_2(NO_3)_4(H_2O)_2].5H_2O$



C6: $[Ni(HL_{II})_2(H_2O)_4].(NO_3)_20.2H_2O$

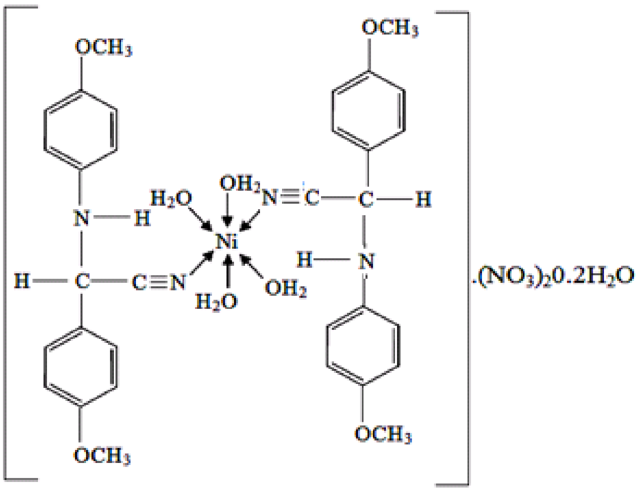


Table (1): Molecular formula physical properties and atomic absorption of metal complexes for HL_I and HL_{II} and their names

Symbol	Molecular formula (colour) Names	m.p˚C	Yield%	M% Found (calc.)
HL_I	$C_{16}H_{16}N_2O$ (Yellow) (p-methyl anilino)-p-methoxy phenyl acetonitrile	95-96	70	-
C_1	$[Ni(HL_I)_2](NO_3)_2$ (greenish yellow) [bis{(p-methyl anilino)-p-methoxy phenyl acetonitrile} nickel (II)] nitrate	250-252	55	9.11 (8.55)
C_2	$[Co(HL_I)_2](NO_3)_2$ Yellow [bis{(p-methyl anilino)-p-methoxy phenyl acetonitrile} cobalt (II)] nitrate	248 Decomp.	50	8.11 (8.58)
C_3	$[FeL_INO_3(H_2O)_2].NO_3.2.2\ H_2o$ (dark brown) [Nitrato-diaqua{(p-methyl anilino)-p-methoxy phenyl aceto nitrile} ferric (III)] nitrate. (2.2) Hydrate	230 Decomp.	45	11.04 (11.02)
HL_{II}	$C_{16}H_{16}N_2O_2$ (brown) (p-methoxy anilino)-p-methoxy phenyl acetonitrile	103-104	60	-
C_4	$[Cu_2(L_{II})_2(H_2O)_8](NO_3)_2$ (dark brown) [Octaaqua-di-μ-{(p-methoxy anilino)-p-methoxy phenyl acetonitrile} dicopper(II)] nitrate	> 270	42	13.42 (13.67)
C_5	$[Fe_2(L_{II})_2(NO_3)_4(H_2O)_2].\ 5H_2O$ (dark brown) [Tetra -nitrato-diaqua-di-μ-{(p-methoxy anilino)-p-methoxy phenyl acetonitrile} diferric(III)] (5) Hydrate	> 270	33	10.42 (10.93)
C_6	$[Ni\ (HL_{II})_2\ (H_2O)_4](NO_3)_2.0.2\ H_2O$ (greenish brown) [Tetraaquabis{(p-methoxy anilino)-p-methoxy phenyl acetonitrile} nickel (II)] nitrate. (0.2) Hydrate	240-242	59	10.73 (10.68)

Table (2): Characterterstic Stretching vibrations υ (cm^{-1}) of i.r. spectra for ligands and their metal complexes

Symbol	υ_{N-H}	$\upsilon_{C\equiv N}$	υ_{H2O} Lattice (coordinate)	$\upsilon_{M-N\equiv C}$	υ_{M-N}	υ_{M-O}	υ_{NO3}	γ-CH out of plane
HL_1	3360	2220	-	-	-	-	-	840 740 700
C_1 Ni(II)	3230	2400 2164	-	446	(295)^b	-	1750 - 1645^e	833
C_2 Co(II)	3352	2172	-	412	(289)^b	-	1750- 1660^e	870 785 750
C_3 Fe(III)	-	2430	3414 (694)	428	(356)^a	(316)^c (298)^d	(1670)^e 1415 1364^g	785 725 775
HL_{II}	3320	2220	-	-	-	-	-	840 790 740
C_4 Cu(II)	-	2300 2137	(650) (600)	467	(353)^a	(320)^c	1750 1650^e	839 745 700
C_5 Fe(III)	-	2370	3454 (704)	467	(357)^a	(312)^c (285)^d	(1512)^f 1366 1312^g	830 780 700
C_6 Ni(II)	3422	2200 2168	3500 650 615	448	-	390^c 353	(1750)^e	833 756

Where : a = υ_{M-N}, b=υ_{M-NH} , C = υ_{M-OH2} d=υ_{M-ONO2}, e=Free ion NO^-_3 , f = monodentate of NO^-_3, g =bidentate of NO^-_3

Table (3): Electronic spectral data, electrical conductivities (DMF 10^{-3}M), Magnetic susceptibilities (μ_{eff}B.M) and suggested geometries for metal complexes of HL_I and HL_{II}

symbol	Maximum absorption υ_{max} (cm^{-1})	Band assignment	Dq/B`	B` cm^{-1}	β	10Dq	υ_2/υ_1	Molar conductivity in DMF S. mol^{-1}cm^{2}	μ_{eff} B.M	Suggested structure
HL_I	31447	$\pi \rightarrow \pi^*$	-	-	-	-	-	-	-	-
C_1 Ni(II)	υ_1 14286 υ_2 18750	$^1A_1g \rightarrow {}^1A_2g$ $^1A_1g \rightarrow {}^1B_1g$	-					165	Diamagnetic	Square planar
C_2 Co(II)	υ_1 6266 (cal.) υ_2 10256 υ_3 17092(avr) υ_4 27777	$^4A_2 \rightarrow {}^4T_2(F)$ $^4A_2 \rightarrow {}^4T_1(F)$ $^4A_2 \rightarrow {}^4T_1(P)$ L $\rightarrow$ M (C.T)	1.1	570	0.587	6270	1.64	145	3.81	Tetrahedral
C_3 Fe(III)	υ_1 15974 υ_2 18750 υ_3 23077 υ_4 26366 υ_5 28000	$^6S(A_1g) \rightarrow {}^4G\ ({}^4T_2g)$ $^6A_1g \rightarrow {}^4T_1g$ L $\rightarrow$ M (C.T) $\left.\begin{matrix}\pi \rightarrow \pi^* \\ \pi \rightarrow \pi^*\end{matrix}\right\}$ C.T intraligand	-	-	-	-	-	57	5.57	Octahedral
HL_{II}	υ_1 27419 υ_2 32075	$n \rightarrow \pi^*$ $\pi \rightarrow \pi^*$	-	-	-	-	-	-	-	-
C_4 Cu(II)	υ_1 12376 υ_2 15385 υ_3 18181	$^2B_1g \rightarrow {}^2A_1g$ $^2B_1g \rightarrow {}^2B_2g$ $^2B_1g \rightarrow {}^2Eg$	-	-	-	-	-	170	1.89	Octahedral
C_5 Fe(III)	υ_1 10072 υ_2 18868	$^6S({}^6A_1g) \rightarrow {}^4G\ ({}^4T_2g)$ $^6A_1g \rightarrow {}^4T_1g$	-	-	-	-	-	30	3.89	Octahedral
C_6 Ni(II)	υ_1 10256 υ_2 14815 υ_3 23333 (cal.) υ_4 27274	$^3A_2g \rightarrow {}^3T_2\ g(F)$ $^3A_2g \rightarrow {}^3T_1g\ (F)$ $^3A_2g \rightarrow {}^3T_1g\ (P)$ L $\rightarrow$ M (C.T)	2.06	4.92	0.48	10135	1.44	174	3.78	Octahedral

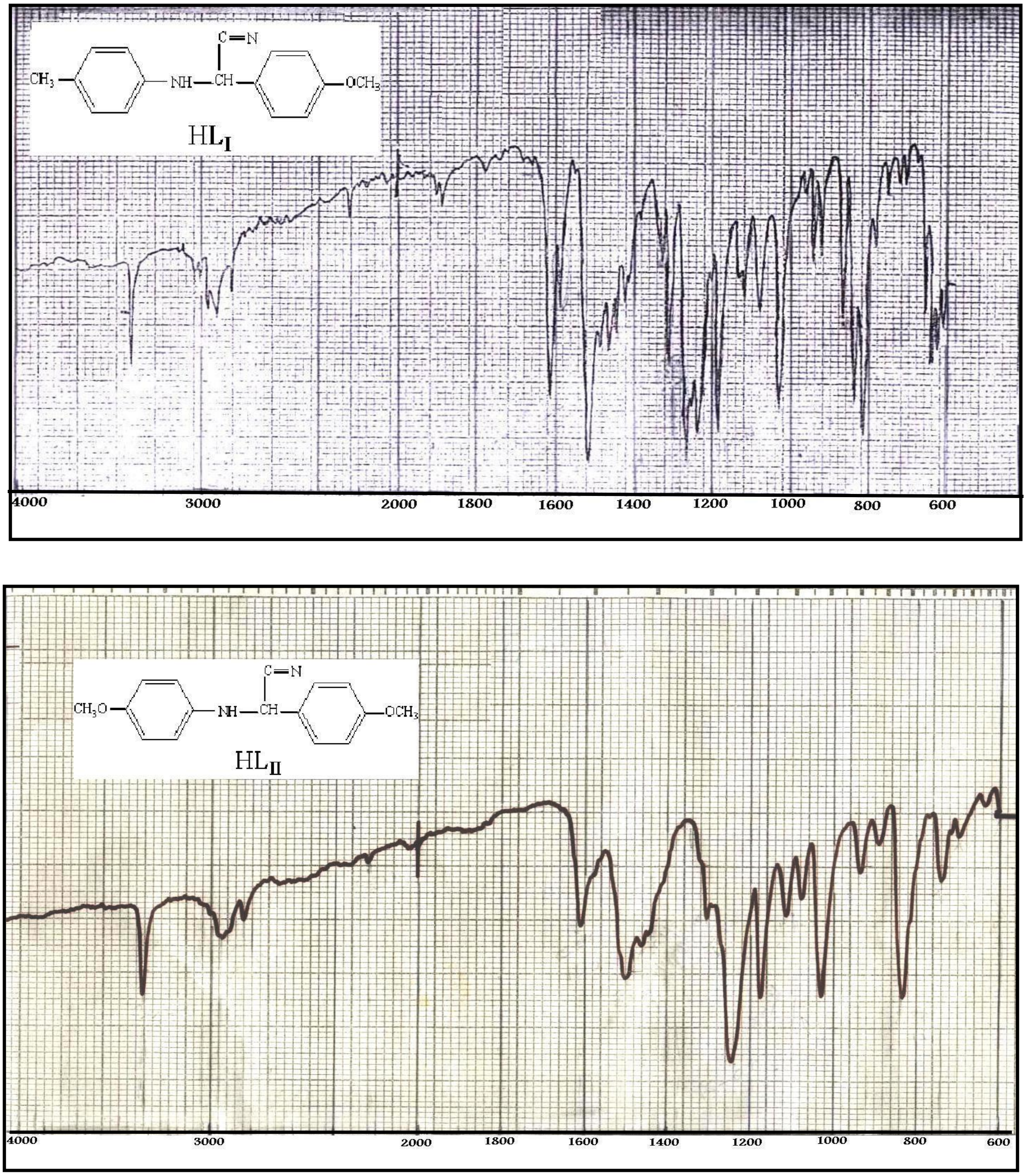
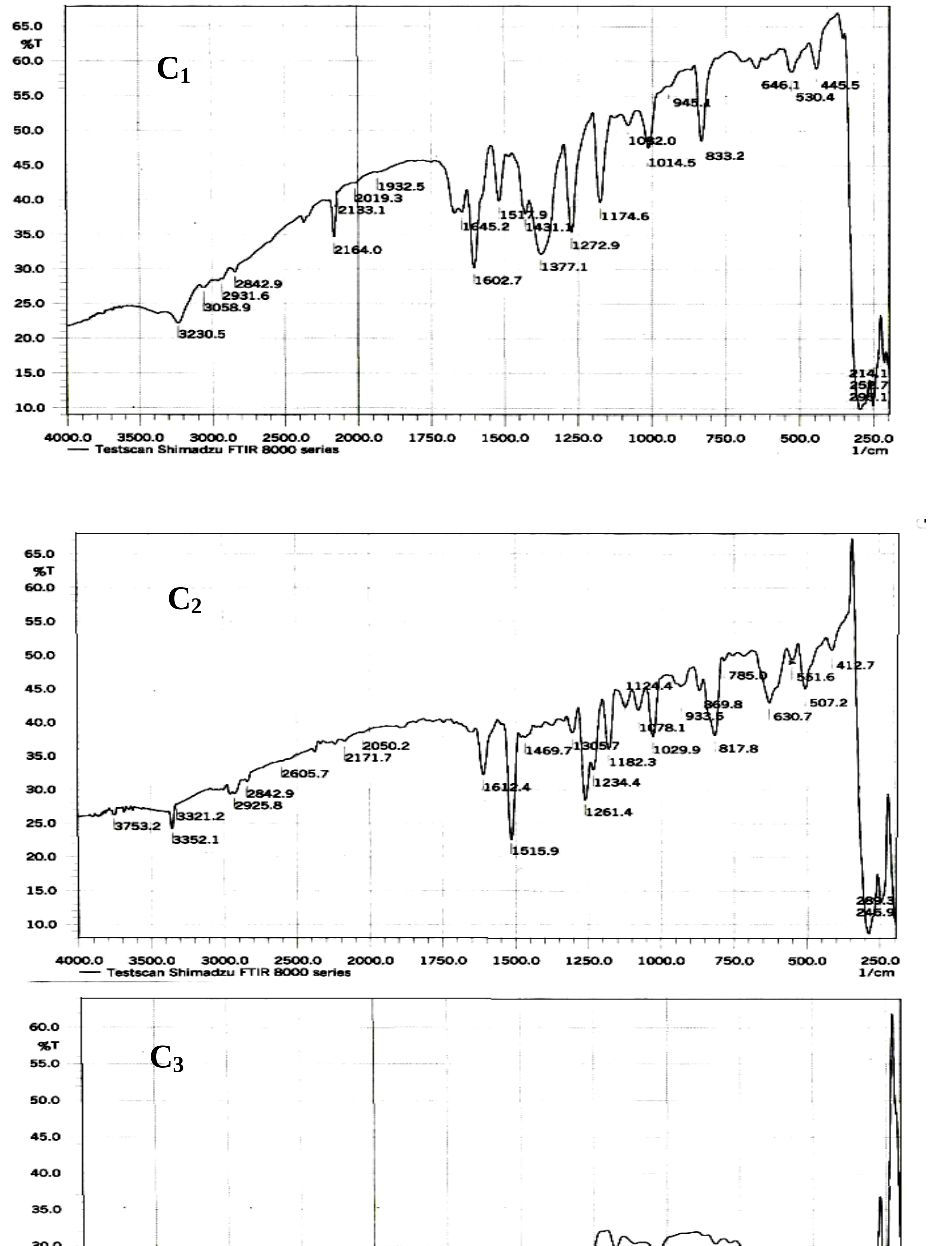


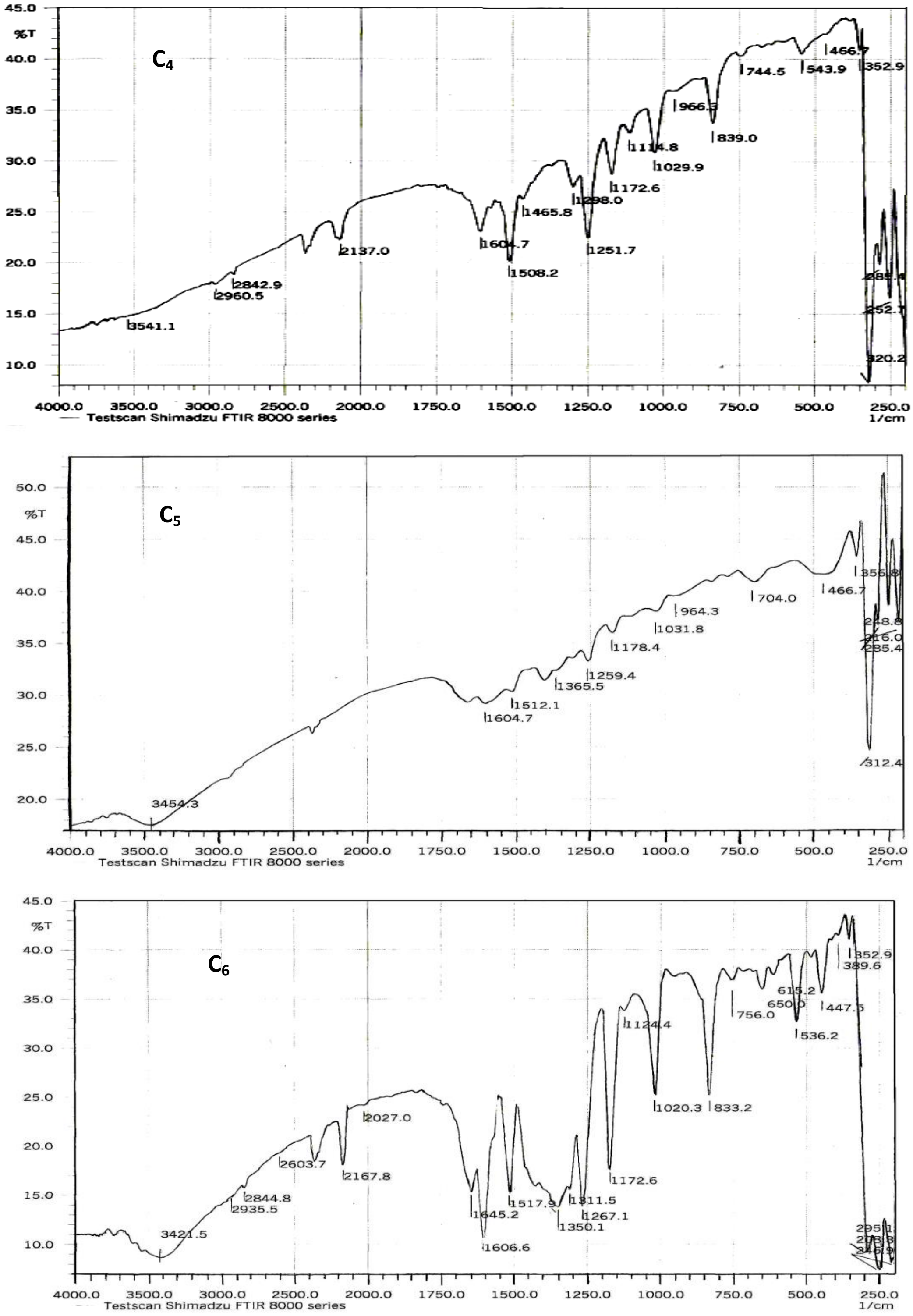
Fig. (1) : I.R spectra of HL_I and HL_{II}

Fig. (1) : continued



FTIR Spectra of HL_I complexes C_1:Ni(II), C_2:Co(II) and C_3:Fe(III)

Fig. (1) : continued



FTIR Spectra of HL_{II} complexes C_4:Cu(II), C_5:Fe(III) and C_6:Ni(II).

Fig. (2): Electronic Spectra of HL_I and HL_{II} and their metal complexes C_1:Ni(II), C_2:Co(II), C_3:Fe(III), C_4:Cu(II), C_5:Fe(III) and C_6:Ni(II),

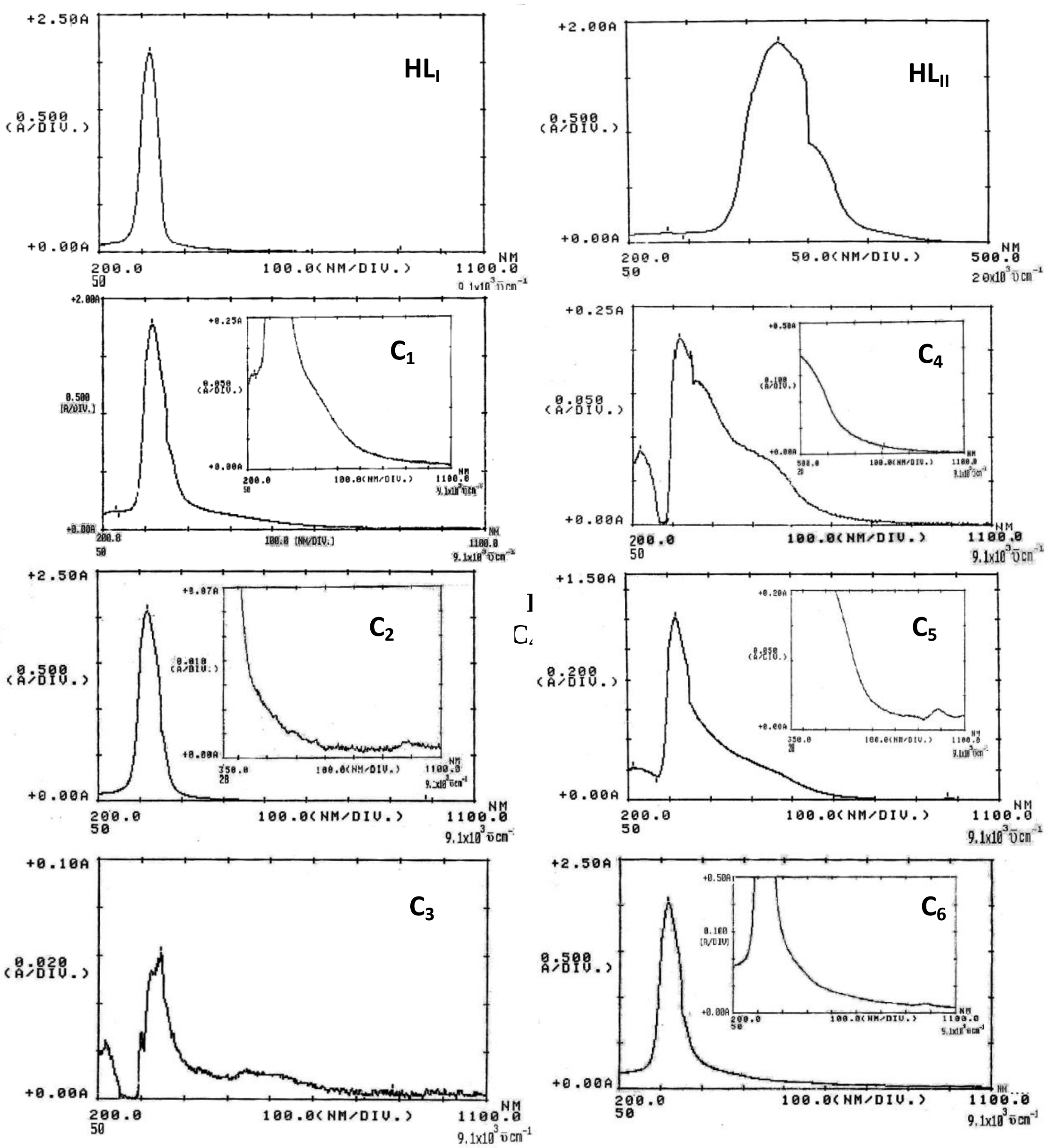


Fig. (2): Electronic Spectra of HL$_I$ and HL$_{II}$ and their metal complexes C$_1$:Ni(II), C$_2$:Co(II), C$_3$:Fe(III), C$_4$:Cu(II), C$_5$:Fe(III) and C$_6$:Ni(II),