Synthesis, Characterization, of mixed ligand Complexes of (Anthranilic Acid and Nicotinamide) with Mn(II), Co(II),Ni(II), Cu(II), Zn(II) Cd(II), Hg(II) *and* pd(II)

تحضير وتشخيص معقدات مختلطة الليكاند من (حامض الانثرانيلك والنيكوتين امايد) مع Mn(II),Fe(II),Co(II),Ni, Cu(II), Zn(II) Cd(II), Hg(II) *and* pd(II)

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الخلاصة

يتضمن البحث تحضير وتشخيص المعقدات المختلطة الليكاند للايونات M^{+2} باستعمال الحامض الاميني (حامض الانثرانيلك) ليكاند أولي و(النيكوتين أمايد) ليكاند ثاني بالصيغة العامة:$M(NA)_2(A)]\ Cl$[إذ ان حامض الانثرانيلك ($C_7H_7NO_2$) بالرمز (AH) و النيكوتين أمايد ($C_6H_7N_2O$) بالرمز(NA) وذلك بمفاعلة الليكاندين مع كلوريدات العناصرباستعمال الايثانول مذيباً وفي درجة حرارة المختبروبنسبة مولية [(1:2:1)(metal:2NA : A^-)] مع M(II) إذ أن:

M(II)= Mn(II), Co(II),Ni(II), Cu(II), Zn(II) Cd(II), Hg(II) *and* pd(II)

يسلك الليكاند حامض الانثرانيلك [(الفاقد بروتون والمتحول إلى أيون الانثرانيليت (A^-) باستعمال القاعدة (NaOH) كليكاند ثنائي السن، إذ يرتبط بالأيون المركزي عن طريق ذرة الأوكسجين في مجموعة الكاربوكسيل ($-COO^-$) وذرة النتروجين في مجموعة الأمين (NH_2) بينما يسلك النيكوتبن امايد كليكاند أحادي السن إذ يرتبط من خلال ذرة النتروجين.

Abstract

The research includes the synthesis and identification of type mixed ligand complexes of M^{+2} Ions using amino acid (anthranilic acid) a primary ligand and nicotinamide as secondary ligand. The mixed ligand complexes of composition, $Cl\ [M(NA)_2(A)]$
Where anthranilic acid ($C_7H_7NO_2$) symbolized as AH and nicotinamide($C_6H_7N_2O$) symbolized (NA) .The ligand and the metal chlorides were brought in to reaction at room temperature in ethanol as solvent .The reaction required the following molar ratio]$^-$) [(1:2:1)(metal:2NA : A^-]with M^{+2} ions, where

M(II) = Mn(II), Co(II),Ni(II), Cu(II), Zn(II) Cd(II), Hg(II) *and* pd(II)

The results showed that the deprotonated ligand(anthranilc acid) to anthranilate ion (A^-) by using (NaOH) coordinated to metal ions as bidentate ligand through the oxygen atom of the carboxylate group ($-COO^-$), and the nitrogen atom of the amine group (NH_2), where the nicotinamide coordinated as a monodentate through the nitrogen atom.

Introduction:

Nicotinamide (NA) is a form of niacin is very prevalent in plants and human tissues a deficiency of this vitamin leads to loss of copper from the body, known as pellagra disease. The Nicotinamide (3-pyridine carboxamide) is a pyridine derivative which is important bio ligand for human health. [1]

In the recent decade, the synthesis and structure of new series of bimetallic complexes with A has been studied by various methods because of biological importance of NA [2]. Although the synthesis, characterization and electrochemical behavior of complexes of nicotinamide with some metal ions (Cu(II), Co(II), Ni(II), Pb(II), Cr(III) and Zn(II)) were studied [3–6]

A series of mixed ligand containing nicotinamide and saccharinato complexes [7-9]
the thermodynamic and electrical properties of amino phenol and o-amino-benzoic acid (anthranilic acid) complexes with Mn(II), Fe(II), Co(II), Ni(II) and Cu(II). Several techniques such as conduct metric and photometric titrations, IR spectra, thermal analysis and X-ray diffraction were used to characterize the composition of complexes. [9]

There are many reports on the metal-anthranilate complexes along with the structure of many of these compounds . Some transition metal anthranilate have capability for aren't hydrogenation . [10-12]

In this paper we present the synthesis and study of metal complexes contain mixed Ligands of Anthranilic Acid as a primary and Nicotinamide as secondary ligand .

Experimental:

a- chemicals:

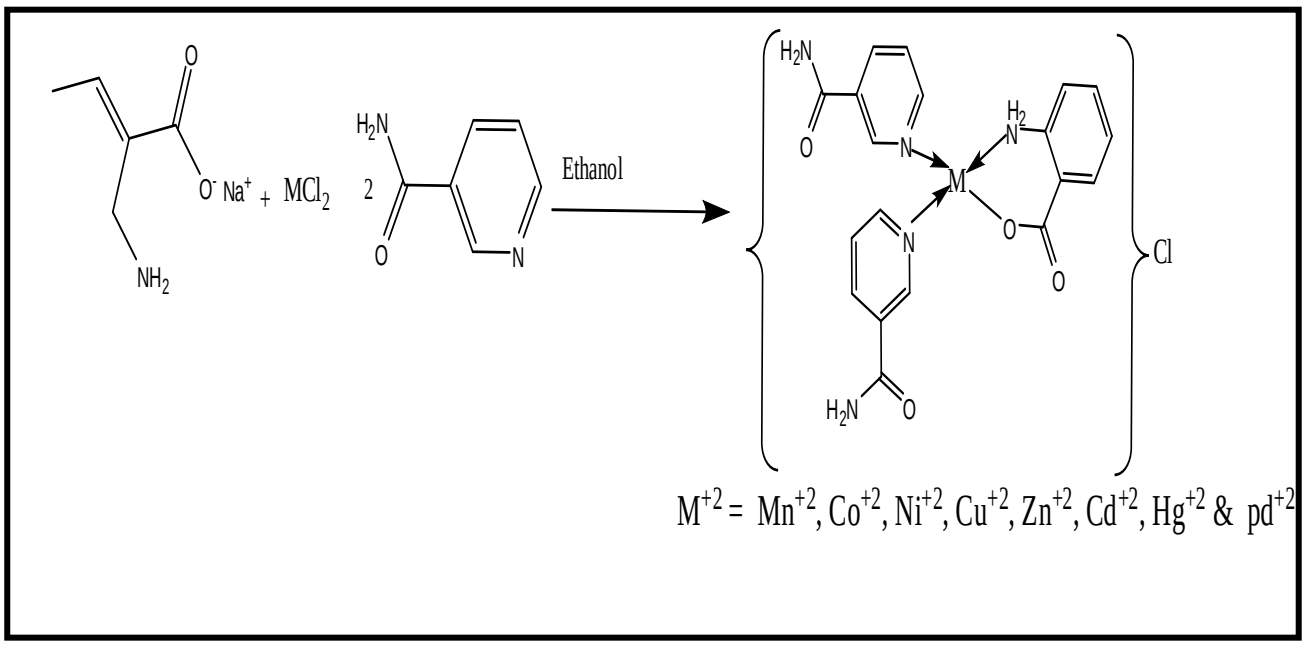
Anthranilic Acid and Nicotinamide were purchased from (Merck),solvents and all the metal ions M^{+2} = Mn^{+2}, Co^{+2}, Ni^{+2}, Cu^{+2}, Zn^{+2}, Cd^{+2}, Hg^{+2} & pd^{+2}. were of Analar grade (BDH). They were used in the form of chlorides without any further purification.

b- Instruments:

FT-I.R spectra were recorded as KBr discs using Fourier transform Infrared Spectrophotometer Shimadzu 24 FT-I.R 8400s.
Electronic spectra of the prepared complexes were measured in the region (200- 1100) nm for 10^{-3} M solutions in DMF at 25ºC using shimadzu-U.V-160 . A Ultra Violet Visible Spectrophotometer with 1.000 ± 0.001 cm matched quartz cell. While metal contents of the complexes were determined by Atomic Absorption (A.A)Technique using Japan A.A-67G Shimadzu .
Elemental Analysis (C.H.N.) was carried out with: Perkin Elmor B-240 Elemental Analyzer.
Electrical conductivity measurements of the complexes were recorded at 25ºC for 10^{-3} M solutions of the samples in DMF using pw9527 Digital conductivity meter (Philips).
Magnetic susceptibility measurements were measured using Bruker magnet BM6.Melting points were recorded by using Stuart melting point apparatus. The proposed molecular structure of the complexes were determinated by using chem. office prog, 3DX (2006).

B: General procedure: Synthesis of the complexes

1- Nicotine amide solution :prepared by dissolve [(0.224 gm) 2m.mol] in ethanol (10ml).
2- Sodium anthranilate ($Na^{+}Anth^{-}$) was prepared by a naturalization of anthranilic acid (AH)[0.137gm(1mmol)] ethanolic solution with [0.04 gm(1mmol)]of sodium hydroxide ethanolic solution .
3- Synthesis of complexes: An aqueous solution of the metal salt was added to the solution of the ligands in ethanol respectively using stoichiometric amounts (1:2:1)(metal: ligand: ligand)(M:2NA: Na^{+} $Anth^{-}$) molar ratio, the mixture was stirred for half an hour at room temperature, crystalline precipitates observed. The resulting precipitates were filtered off ,recrystallized from ethanol and dried at room temperature according to the following reaction : (scheme1) :



Scheme (1): Synthesis of the [M ($C_{19}H_{18}N_5O_4$)] Cl complexes

Results and Discussion:

Physical properties of the prepared complexes:

Table (1) shows the physical data for the prepared complexes which show different melting points, all of them were higher than the two ligands, All the complexes are colored, non-hygroscopic and thermally stable solids (Table 1), indicating a strong metal-ligand bond. The complexes are insoluble in water but soluble in common organic solvents such as ethanol, ethyl alcohol, acetone, chloroform ,DMF and DMSO solvents. The elemental analysis(C.H.N) were found to be in agreement with calculated values. Table (1) includes the physical properties and elemental analysis. The analytical data confirmed the (1:2:1) (M:2NA: Na^+ $Anth^-$) composition of the complexes.

Molar conductance:

The molar conductance values of the complexes in DMF at 10^{-3} M concentration at 298^0K Table (1) are found to be (52.7-80.6) μS.cm^{-1}, for complexes of composition [M (A) $(NA)_2$]Cl indicating their electrolytic nature correspond to 1:1 electrolytes. [13 -14]

Atomic Absorption :

The atomic absorption measurements (Table 1) for all complexes gave approximated values for theoretical values.

In conclusion, our investigation this suggest that the ligands Anthranilic Acid and 1- Nicotinamide coordinate with M (II) forming tetrahedral geometry (Figure 2) while Pd(II) complex is square planer .

The electronic spectra :

The electronic spectra of all compounds (Ligands and complexes) are listed in Table (2) figures(4-6) together with the proposed assignments and suggested geometries.

The spectrum of the free ligand (AH) in DMF solvent shows a high intensity band in wave length 337 nm (29673cm^{-1})(2337.mol^{-1}.cm^{-1}) assigned to($\pi \rightarrow \pi^*$) and in wave length 360 nm (27777cm^{-1}) ε_{max} (1108 l.mol^{-1}.cm^{-1}) assigned to ($n \rightarrow \pi^*$).(ff) and free ligand (nicotinamide) (NA) shows a high intensity band in wave length 276 nm (3623 cm^{-1}) max (626 l.mol^{-1}.cm^{-1}) assigned to ($\pi \rightarrow \pi^*$) Fig1 [14] in addition to these transitions the spectra of the complexes

exhibited another new bands in the visible region caused by charge transfer (C.T) assigned to (d-d) transitions between the metal ion and the ligands . [15-16]

$[Cu(C_{19}H_{18}N_5O_4)]$ Cl (d^9) : The pale green complex of Cu(II) gave band at wave number (41841)cm^{-1} caused by (C.T) transition and only one absorption band was observed in the visible region at (18832) cm^{-1} which originated to (d-d)electronic transition type [$^2B_1 \rightarrow {}^2E_1$] ,apposition of this peak is a good agreement with reported for Cu(II) distorted tetrahedral geometry [17]

$[Zn(C_{19}H_{18}N_5O_4)]Cl$,$[Cd(C_{19}H_{18}N_5O_4)]Cl$ and $[Hg(C_{19}H_{18}N_5O_4)]Cl$: ($d^{10}$)(white complexes) : Because of filled d- shell of these complexes, no ligand field absorptions band was observed, therefore the bands appeared in the spectra of three complex could be attributed to charge transfer transition. in fact this result is a good agreement with previous work of tetrahedral geometry [18-19]

The μ_{eff} of values for the following high spin tetrahedral complexes were found as complexes for Co (II) (d^7) complex is 4.32 B.M , for Ni(II) (d^8) complex is 4.55 B.M , for Cu (II) complex is 1.35 B.M .While magnetic susceptibility measurements for Cd(II),Hg(II) and Zn(II) (d^{10})(white complexes) showed diamagnetic as expected from their electronic configuration . [19]

The brown palladium complex shows strong change transfer bands which was extended to the visible region , so the ligand field bands could not be established easily. Nevertheless two weak bands at 24629.93 cm^{-1} and at 28490.02 cm^{-1} may be assigned to the transition $^1A_{1g} \rightarrow {}^1B_{1g}$ and $^1A_{1g} \rightarrow {}^1E_{1g}$, respectively, for spin paired d^8 square planner configuration with magnetic moment value of (0.00 BM) . This assignment was made by reference to known palladium complexes with square planar stereochemistry. This is in good agreement with published data [18-19].

Fourier transform infrared spectra :

The analysis of the spectra was performed in comparison with ligand (Sodium anthranilate , nicotinamide).

The assignment of some of the most characteristic FT-IR band of the complexes are shown in (Table -3) together with those of (Sodium anthranilate, and nicotinamide recorded for comparative purposes and facilitate the spectral analysis. Absorption bands in the (648-514)cm^{-1} region are considered to be due to metal-nitrogen vibrations [18,19] whilst those occurring around (418-460)cm^{-1} are thought to arise from metal-oxygen vibration . [20-21]and finally the sharp bands at $(3368\text{-}3405)_{asym}$ cm^{-1} ,$(3161\text{-}3357)_{sym}$ are attributed to the N-H_2 stretching vibration respectively . [22-23]

Nomenclature of prepared complexes:

Table (4) shows empirical formula and nomenclature (IUPAC) with abbreviated.

Proposed molecular structure

Studying complex on bases of the above analysis, shows the existence of tetra coordinated $[M(NA)_2(A)]$, M = Mn^{+2}, Co^{+2}, Ni^{+2}, Cu^{+2}, Zn^{+2}, Cd^{+2}, Hg^{+2} & pd^{+2} .The proposed structure of the prepared complexes are drawn as Figure. (9) using, (Chem. Office– Cs– 3D program 2006) 3DX (2006).

Table (1) Analytical data and some physical properties of the ligands and their complexes.

Compounds	M.wt	M.p (de) °c	Color	Λ_m $\mu S.cm^{-1}$	(C.H.N)			
					C	H	N	Metal %
Nicotinamide (NA)	122.12	133	White	2.3	-	-	-	-
Anthranilic (AH)	137.14	146	Pale-yellow	6.2	-	-	-	-
$[Mn(C_{19}H_{18}N_5O_4)]Cl$	435.32	220	Brown	52.7	52.42 (51.88)	4.17 (3.88)	16.09 (16.00)	12.62 (11.96)
$[Co(C_{19}H_{18}N_5O_4)]Cl$	439.31	276	Bink	54.5	51.95 (50.16)	4.13 (4.12)	15.94 (15.30)	13.41 (12.86)
$[Ni(C_{19}H_{18}N_5O_4)]Cl$	439.07	230	Pale-green	70.7	51.97 (52.96)	4.13 (4.12)	15.95 (16.11)	13.37 (14.12)
$[Cu(C_{19}H_{18}N_5O_4)]Cl$	443.92	225	Pale-green	66.8	51.41 (50.30)	4.09 (4.12)	15.78 (15.90)	14.31 (14.99)
$[Zn(C_{19}H_{18}N_5O_4)]Cl$	445.77	270	White	60.8	51.19 (50.82)	4.07 (4.86)	15.71 (15.86)	14.67 (14.90)
$[Cd(C_{19}H_{18}N_5O_4)]Cl$	492.79	287	White	69.4	46.36 (45.60)	3.68 (2.66)	14.21 (13.24)	22.81 (21.66)
$[Hg(C_{19}H_{18}N_5O_4)]Cl$	580.97	287	Pale-green	65.5	39.28 (39.20)	3.12 (2.86)	12.05 (12.00)	34.53 (---)
$[Pd(C_{19}H_{18}N_5O_4)]Cl$	486.8	295	Brown	80.6	46.83 46.70	3.69 3.12	14.37 13.30	12.62 (---)

Λ_m = Molar Conductivity , M.p= Melting points

Table (2) Electronic Spectra of the tow ligands and there complexes

Compound	λ_{nm}	$\upsilon'_{cm^{-1}}$	ξ_{max} L.mol^{-1}.cm^{-} 1	Assignment	Probable Figure
(NA)	280 276	35714.28 3623.88	1880 629	$\pi\rightarrow\pi^*$ $\pi\rightarrow\pi^*$	
(AH)	277 304	36101 32894	343 391	$\pi\rightarrow\pi^*$ $n\rightarrow\pi^*$	
$Mn(C_6H_6N_2O)_2$ $(C_7H_6NO_2)$	296 327 570	33783.78 30581.40 1713.86	550 1486 60	Ligand field Charge transfer $^4T_{1\,(P)} \rightarrow {}^4A_{\,1}$	Tetrahedral
$Co(C_6H_6N_2O)_2$ $(C_7H_6NO_2)$	294 360	34013.60 27777.77	27473 1106	Ligand field $^4A_{\,2\,(f)} \rightarrow {}^4T_{1(P)}$	Tetrahedral
$Ni(C_6H_6N_2O)_2$ $(C_7H_6NO_2)$	230 291	34364.26 43478.26	2469 250	C.T C.T	tetrahedral
$Cu(C_6H_6N_2O)_2$ $(C_7H_6NO_2)$	239 531	41841 18832	2453 244	C.T $^2B_1\rightarrow {}^2E_1$	distorted tetrahedral
$Zn(C_6H_6N_2O)_2$ $(C_7H_6NO_2)$	281 316	35587.18 31645.56	933 2500	C.T C.T	Tetrahedral
$Cd(C_6H_6N_2O)_2$ $(C_7H_6NO_2)$	310	32258.06	2215	C.T	Tetrahedral
$Hg(C_6H_6N_2O)_2$ $(C_7H_6NO_2)$	272	36900.36	1398	C.T	Tetrahedral
$Pd(C_6H_6N_2O)_2$ $(C_7H_6NO_2)$	291 351 406	34364.26 28490.02 24629.93	2475 895 907	C.T $^1A_1\rightarrow {}^1E_1$ $^1A_1\rightarrow {}^1B_1$	Sq.p

Compound	NH_{2asy} str	NH_{2sym} str	$CH_{(py)}$ str	C=O Str (amid)	NH_2(def) (am)	ring str (py)	(C-C) str (py)	C=N Str (am)	i.p(CH) (py)	o.p(CH) (py)	O=CN Bend(am)	υ (-coo⁻) asym	υ (-coo⁻) sym	M-N	M-O
Nicotinamide (na)	3368 vs	3161s	3060 sh	1679 vs 1697 sh	1618 vs	1592 vs	1423 vs 1123 m	1395 vs	1230 vw 1090 vw	936 vw 829 m	736 vs	–	–	–	–
Anthranilic (A)	3380 s	3330vs	–	1682 m	–	–	–	–	–	–	–	1650s	1400 s	–	–
[Pd(NA)$_2$A]Cl	3384w	3357w	3315 S	1678m	1628 m	1598 m	1436m	1385 m	–	–	710	1584v w	1406 vw	548	460
[Co(NA)$_2$A]Cl	3307vs	3251m	3136 S	1670 m	1614 vs	1591 vs	1458s 1190w	1320 m	1260 1039 m	869 s 830 m	752 vs	1537vs	1407 vs	514m	418 m
[Zn(NA)$_2$A]Cl	3365m	3298s	3130 S	1677 m	1616 vs	1591 vs	1458s 1199w	1326 m	1240w 1051 m	869 s 811 w	754 s	1541vs	1406 vs	514s	414 m
[Mn(NA)$_2$A]Cl	3402m	3330m	3190 S	1668 m	1623 vs	1589 vs	1406s 1199w	1383 m	1240 w 1000 w	968 vw 850 m	752 s	1542vs	1444 vs	648m	430 m
[Ni(NA)$_2$A]Cl	3405m	3267m	3124 S	1670 m	1614 vs	1593 vs	1483w	1326 m	1242 m 1095 m	869s	756 vs	1541vs	1406 vs	568m	450 m
[Cu(NA)$_2$A]Cl	3402s	3274`m	3159 S	1630 m	1622 vs	1604 vs	1430w	1379 m	1232 m 1023 m	925m 875m	756 vs	1604 s	14030 s	520m	450
[Cd(NA)$_2$A]Cl	3523m	3288s	3136 S	1636 m	1618 vs	1589 vs	1488s 1166w	1354 s	1166 w 1081 m	905 m 864	756 vs	1537vs	1400 vs	518m	408
[Hg(NA)$_2$A]Cl	3390m	3244m	3178 S	1670 S	1622 vs	1600 vs	1436s 1149w	1373 vs	1220	938 m 830 m	744 s	1552vs	1436 s	551 s	450 m

Table (3)FT-IR spectral data of the Ligands and their Complexes

Table(4) Empirical formula and Nomenclature (IUPAC) with abbreviated

Empirical formula	Nomenclature	Abbreviation
$[Mn(C_6H_6N_2O)_2 (C_7H_6NO_2)]Cl$	Anthranilato bis (nicotinamide) manganese (II) chloride	$[Mn(na)_2A]Cl$
$[Co(C_6H_6N_2O)_2 (C_7H_6NO_2)]Cl$	Anthranilato bis (nicotinamide) cobalt (II) chloride	$[Co(na)_2A]Cl$
$[Ni(C_6H_6N_2O)_2 (C_7H_6NO_2)]Cl$	Anthranilato bis (nicotinamide) nickel (II) chloride	$[Ni(na)_2A]Cl$
$[Cu(C_6H_6N_2O)_2 (C_7H_6NO_2)]Cl$	Anthranilato bis (nicotinamide) copper (II) chloride	$[Cu(na)_2A]Cl$
$[Zn(C_6H_6N_2O)_2 (C_7H_6NO_2)]Cl$	Anthranilato bis (nicotinamide) zinc (II) chloride	$[Zn(na)_2A]Cl$
$[Cd(C_6H_6N_2O)_2 (C_7H_6NO_2)]Cl$	Anthranilato bis (nicotinamide) cadimium (II) chloride	$[Cd(na)_2A]Cl$
$[Hg(C_6H_6N_2O)_2 (C_7H_6NO_2)]Cl$	Anthranilato bis (nicotinamide) mercery (II) chloride	$[Hg(na)_2A]Cl$
$[Pd(C_6H_6N_2O)_2 (C_7H_6NO_2)]Cl$	Anthranilato bis (nicotinamide) Palladium (II) chloride	$[Pd(na)_2A]Cl$

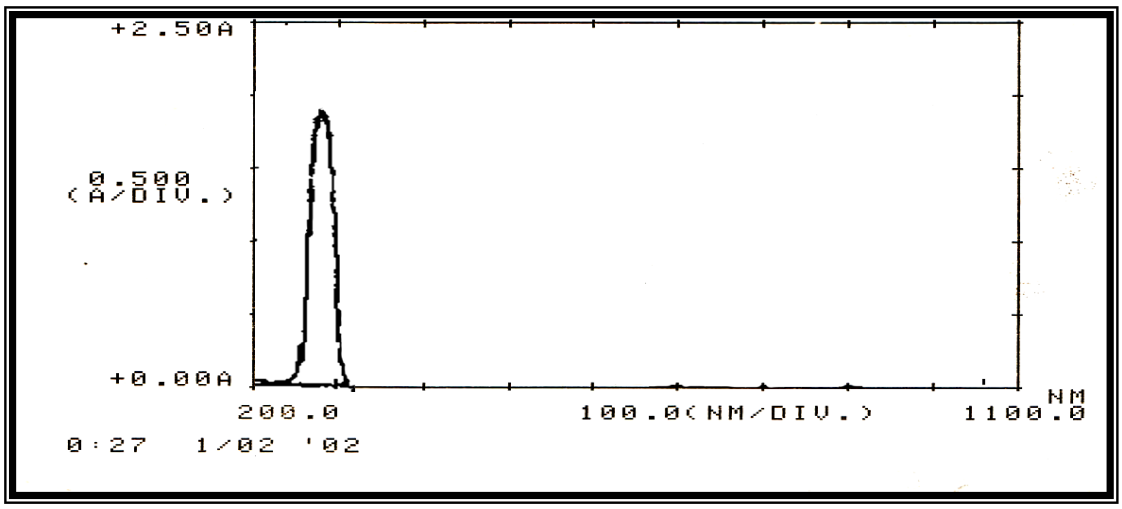


Figure (1) The (UV-Vis) Spectra of $C_6H_6N_2O$

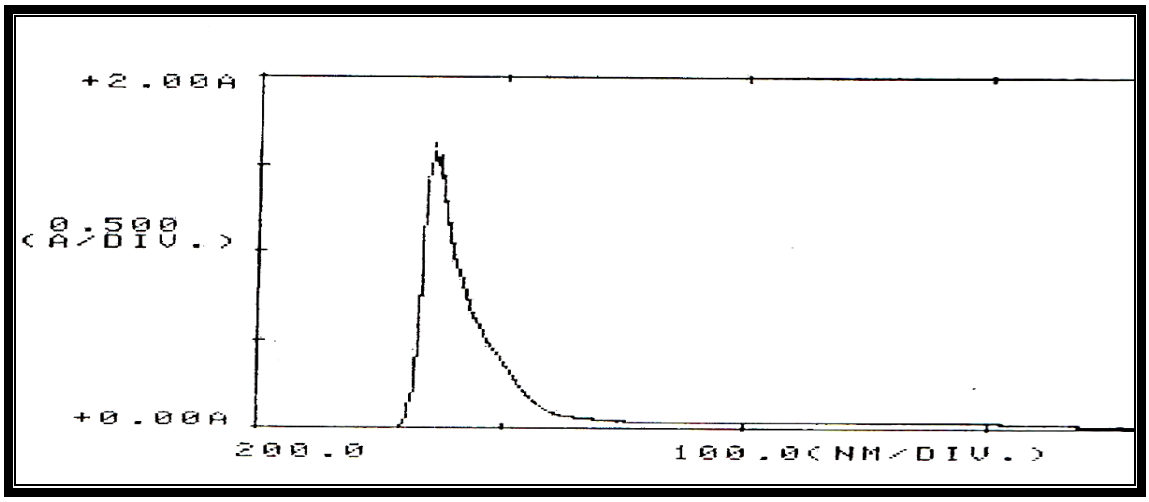


Figure (2) The (UV-Vis) Spectra of $C_7H_7NO_2$

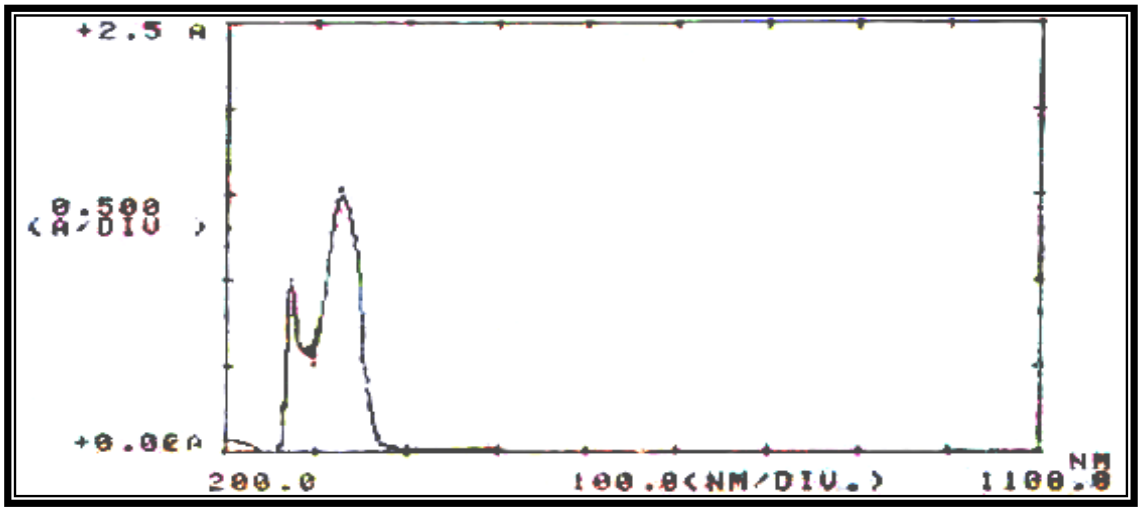


Figure (3) The (UV-Vis) Spectra of $C_{19}H_{18}N_5O_4Mn$

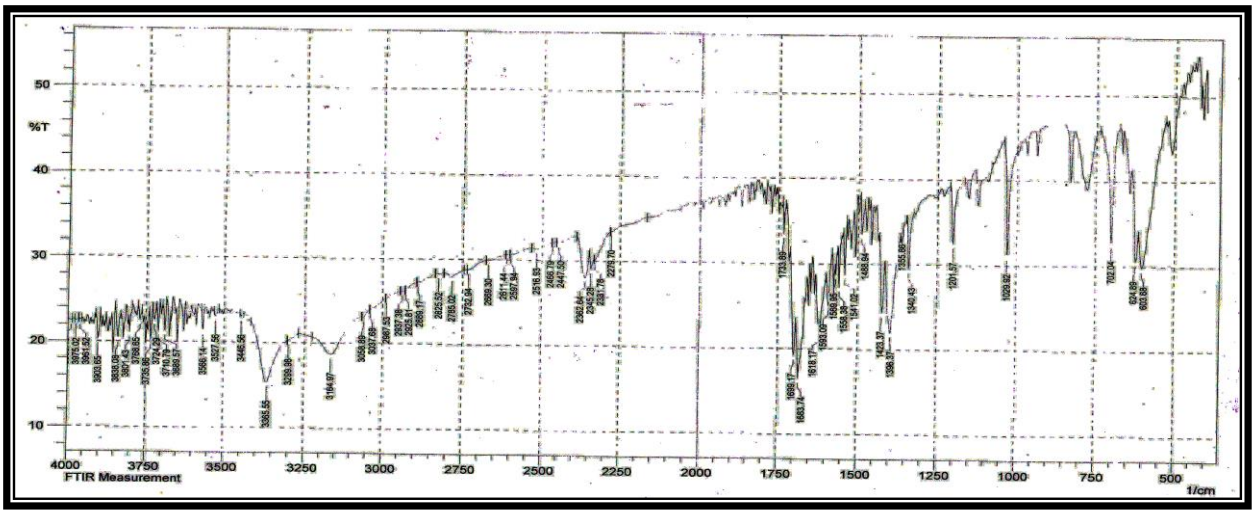


Figure (4) FT IR spectrum of $C_6H_6N_2O$

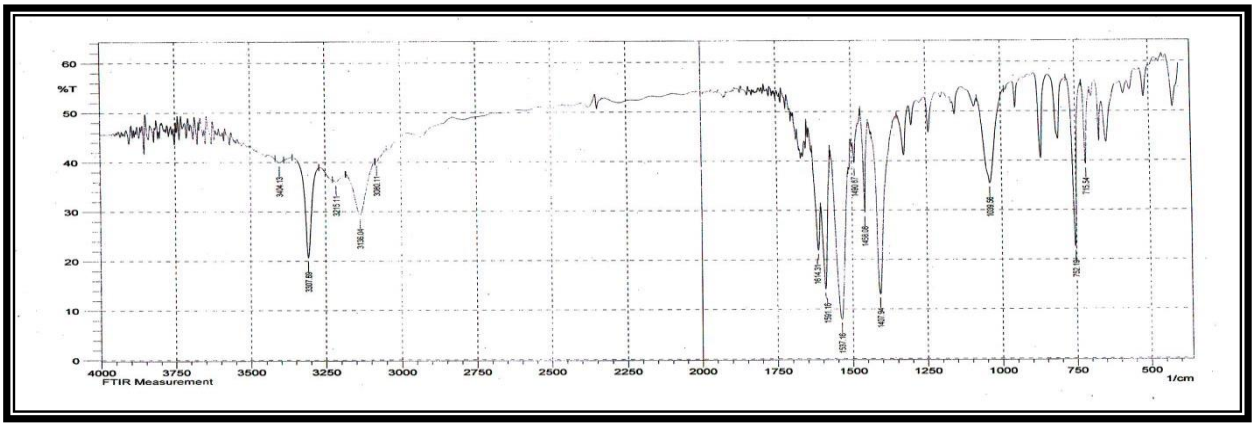


Figure (5) FT IR spectrum of ($C_7H_7NO_2$)

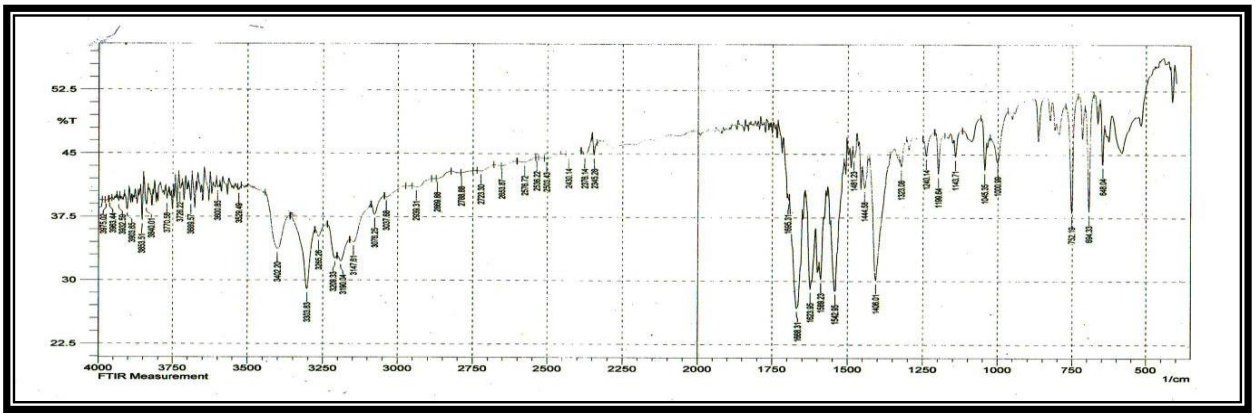


Figure (6) FT IR spectrum of ($C_{19}H_{18}MnN_5O_4$)

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