International Journal of Enhanced Research in Science, Technology & Engineering
ISSN: 2319-7463, Vol. 6 Issue 8, August-2017, Impact Factor: 4.059

Synthesis and Characterization of Some Transition Metal Complexes with (Z)-N1-N6-bis (5-nitropyridine -2-yl) hex-3- enediamide Ligand

Sarah N. Aljarah[1], Maher A.M .Altayy[2]

[1]Department of Chemistry / College of Science / Mosul University / Mosul, Iraq.
[2]Department of Chemistry / College of Education for girls / Mosul University/Mosul, Iraq.

ABSTRACT

New [Mn(II), Fe(II), Co(II), Ni(II), Cu(II)] complexes of N_2O_2tetradentate (Z)-N1-N6-bis(5-nitropyridine-2-yl) hex-3-enediamide symmetric ligand (BNPAH2), prepared by the reaction of 2-butene-1,4-bicarboxylic acid with 2-amino-5-nitropyridine. Also adduct compounds were prepared by the reaction of these complexes with2-amino-5-nitropyridine (ANP)in 1:2(Complex :ANP) molar ratio. The chemical formulae of these complexes are $[M(L)Cl_2]$, $[M(L)(ANP)_2]Cl_2$. When M= Mn(II),Fe(II),Co(II),Ni(II),Cu (II). The ligand and resulting complexes were characterized by analytical, physical and spectral methods. In addition ligand was measured through proton nuclear magnetic resonance technology (^{1}HNMR). These measurements have shown that the ligand acts as neutral tetradentated giving mononuclear complexes with the most probable octahedral structure.

Key Words; Mononuclear transition metal complexes, 5-nitro pyridine complexes, spectral characterization.

INTRODUCTION

Large opened-chain ligands are molecules consisting of a vast number of atoms tied by various bonds forming long branched or non- branched series that have various shapes [1].The most important feature that characterizes these molecules is their high flexibility which enables them to have an attachment with diverse molecules or ions and then result in forming different space shapes [2].The donor multi-atom ligands are used to prepare mono or multi-nuclear complexes containing three or more of the donor atoms linked to one metallic ion. The most common donor atom is the nitrogen, oxygen, sulfur or mixed groups. Large cyclic ligands give a model of four atoms of nitrogen principally positioned at the same level [3]. The large rings with the open chain ligands that contains nitrogen was prepared by using the condensation reaction compounds with metal ion [4],

A lot of metallic complexes are widely studied because of being similar to large compound dysprosium complexes existing in the biological systems [5], Among these complexes that result naturally are the heme found in hemoglobin, cytochromes, catalysis, peroxides and corrin existing in chlorophyll and in vitamin B_{12}. Moreover, from the biological point of view, these compounds have a great importance to life processes. For instance, the metallic proteins use dual-nuclear alkaline to achieve motivational procedures inside the body [6]. The biological activity of many big molecules is confirmed as being antibiotics of various inflammations and cancers in addition to being used in drug manufacturing [7].Besides, these molecules are used in industry for being motivating factors and they may have a lot of promising applications in the future as well [8].

In this study, the new complexes of the metal salts: Mn(II),Fe(II), Co(II), Ni(II), and Cu(II) with BNPAH2 (Z)N1,N6-bis(5-nitropyridine-2-yl) hex-3-enediamide symmetric ligand, which has the chemical forms$[M(BNPAH_2)Cl_2]$ beside preparing adduct complexes with 2-amino-5- nitropyridine (ANP) which have the form of $[M(BNPAH_2)(ANP)_2]CI_2$. The prepared complexes were characterized by elemental analysis molar conductance measurements, magnetic susceptibility measurement, infrared spectra, and electronic spectra studies. Furthermore the ligand(L) is studied by nuclear magnetic resonance (^{1}HNMR).

Experimental

Chemical Materials

All chemical reagents, starting materials as well as solvents were purchased commercially and used without any further purification.

Analytical and Physical Measurements

Elemental analysis of C.H.N. atoms for ligand and complexes (2,4,11) were performed on Elemental Combustion System Costech Instrument set (ECS4010)at Dicle University in Turkey. Melting points or decomposition temperatures for ligand and complexes were measured on Electro thermal Engineering LTD. The molar conductance measurement was carried out in DMF (10^{-3} M) At 25°Cusing conductivity meter model (PCM3 – Jenway).The electronic spectra of complexes were recorded by using Shimadzu, UV- 1650 PC-Spectrophotometer,UV-VIS –Recording at the range (190-1100 nm). For 10^{-3} M solution of compounds in DMF At 25°C using 1cm quartz cell. Magnetic susceptibility of the complexes were measured At25°Cby the Faraday method using Brucker MB6 apparatus. Infrared Spectra of the ligand and its complexes were recorded on FT-IR spectrophotometer, Brucker optics Fourier Transiting Instead (FT-IR) Model (ALPH)at the range 200–400cm^{-1}. Magnetic nuclear ^{1}HNMR spectrum was recorded with 400 MHz on a Bruker AV-1400 model or Bruker AV-1250 model NMR instrument using DMSO-d^{6} as a solvent and TMS at internal standard at the University of Sheffield in England.

Preparation of Open-Chain ligand (BNPAH2)

A mixture of 2-butene-1,4- dicarboxylic acid (0.01mol, 1.44g) and 2-amino-5-nitropyridine(0.02mol, 2.8g) in absolute ethanol 10ml. was heated under reflux with constant stirring for 6 h , The yellow mixture was left for 24h at room temperature, The brown precipitate formed was filtered off, washed several times with cold ethanol, followed by ether and dried under vacuum (Fig1). This ligand had been prepared by a rather different method [9].

Preparation of the Complexes

Preparation of [Mn (BNPAH$_2$)Cl$_2$] Complex

This type of complex was prepared by mixing (0.001mol, 0.197g) of $MnCl_2.4H_2O$ in 10 ml of absolute ethanol with a solution of the ligand (0.001mol, 0.386g) in absolute ethanol 10 ml. The reaction mixture was refluxed with boiling for 2h under constant stirring, on cooling a greenish yellow solid product was filtered, washed several times with cold ethanol, followed by ether and dried in vacuum.

The following complexes[Fe(BNPAH$_2$)Cl$_2$] 0.198g ,$FeCl_2.4H_2O$, [CO(BNPAH$_2$)Cl$_2$] 0.237g, $CoCl_2.6H_2O$, [Ni(BNPAH$_2$)Cl$_2$] 0.236g ,$NiCl_2.6H_2O$, and[Cu(BNPAH$_2$)Cl$_2$] 0.170g $CuCl_2.2H_2O$ Were prepared and isolated in a similar method.

Preparing [Mn(BNPAH$_2$)(ANP)$_2$]Cl$_2$Complex

ANP = 2-amino-5-NitroPyridine

This complex were prepared as follows: (0.001mol, 0.197g) of $MnCI_2.4H_2O$ dissolved in 10ml of absolute ethanol mixed with a solution of(0.001 mol, 0.386 g) ligand in absolute ethanol 10ml and 0.137g 2-amino-5-NitroPyridine dissolved in 10ml of absolute ethanol. The resulting mixture was refluxed with boiling for 2h under constant stirring and on cooling light yellow solid product was precipitated. The resulting product was filtered, washed several times with cold ethanol, followed by ether and dried in vacuum.

The following complexes[Fe(BNPAH$_2$)Cl$_2$] 0.198g ,$FeCl_2.4H_2O$, [CO(BNPAH$_2$)Cl$_2$] 0.237g, $CoCl_2.6H_2O$, [Ni(BNPAH$_2$)Cl$_2$] 0.236g ,$NiCl_2.6H_2O$, and[Cu(BNPAH$_2$)Cl$_2$] 0.170g CuCl2.2H$_2$O Were prepared and isolated in a similar method.

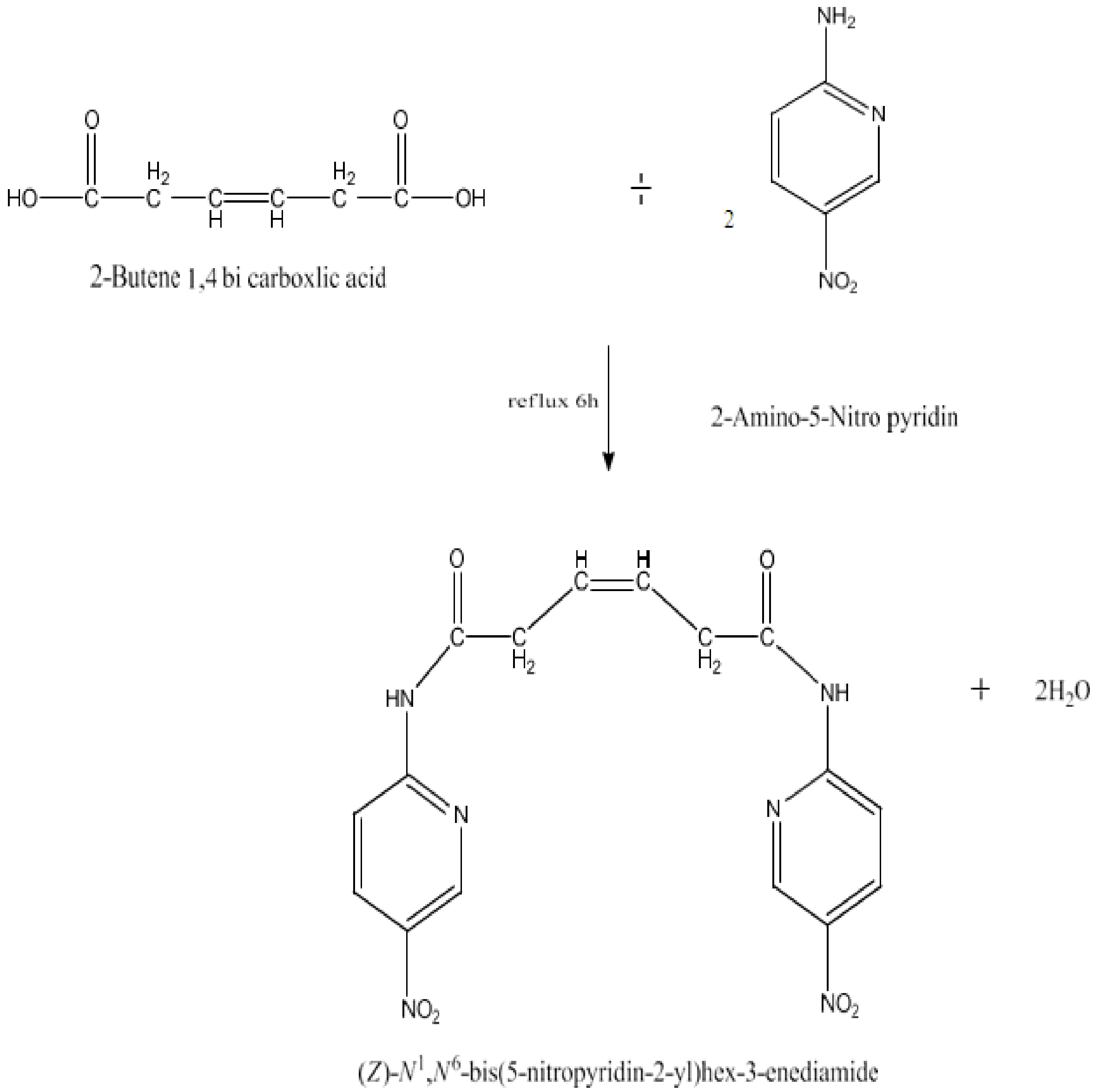

Fig .1: Synthesis of ligand $BNPAH_2$

Results and Discussion

The formation of the transition metal complexes and adduct compounds may be represented by the following chemical equations:

$$MCl_2.nH_2O + \quad BNPAH_2 \longrightarrow \quad [M\,(BNPAH_2)Cl_2] + \quad nH_2O$$

$$MCl_2.nH_2O + BNPAH_2 + 2ANP \longrightarrow [M\,(BNPAH_2)(ANP)_2]Cl_2 + nH_2O$$

M=[Mn(II),Fe(II),Co(II),Ni(II),Cu(II)]

$BNPAH_2$ = represent the ligand (Z)-N^1-N^6-bis(5-nitropyridine-2-yl) hex-3-enediamide.
n= 2,3,6,7.

The analysis data and the results recorded in (Table-1) and the chemical equations mentioned above, it was found that 1:1 metal to ligand (M:L), molar ratio were obtained for all the complexes.

All complexes are colored solids, stable to air at room temperature with neutral charge. They are insoluble in water but they are soluble in dimethyl formamide (DMF) and dimethyl sulfoxide (DMSO).

Table-1: Color, Yield%, Melting Point and elemental analysis for the ligand and its Complexes.

No.	Compound Formulae	Color	melting point(°c)	yield%	ΛM(DMF) ($\Omega^{-1}.mol^{-1}.cm^{2}$)	Elemental analysis% fond (calc.)			
						Cl%	C%	H%	N%
1	($BNPAH_2$)	light yellow	154-156	82	----	---	48.95 (49.74)	3.52 (3.65)	20.92 (21.75)
2	$[Mn(BNPAH_2)Cl_2]$	Greenish yellow	178-175	82	16	13.85 (14.2)	____	___	____
3	$[Fe(BNPAH_2)Cl_2]$	Dark yellow	185-187	73	23	13.82 (12.4)	37.45 (37.14)	2.75 (2.68)	16.37 (16.19)
4	$[Co(BNPAH_2)Cl_2]$	Green	167-168	79	15	13.74 (13.85)	____	___	____
5	$[Ni(BNPAH_2)Cl_2]$	Yellowish green	240-244	80	12	13.74 (14.02)	37.24 (36.94)	2.73 (2.65)	16.28 (16.14)
6	$[Cu(BNPAH_2)Cl_2]$	Dark olive	210-211	75	22	13.62 (14.2)	____	___	____
7	$[Mn(BNPAH_2)(ANP)_2]\ Cl_2$	Light yellow	257-259	76	153	9.88 (10.13)	____	___	____
8	$[Fe(BNPAH_2)(ANP)_2]\ Cl_2$	Light brown	180-182	81	167	9.87 (10.33)	____	___	____
9	$[Co(BNPAH_2)(ANP)_2]\ Cl_2$	Dark green	230-232	84	149	9.95 (10.06)	____	____	____
10	$[Ni(BNPAH_2)(ANP)_2]\ Cl_2$	Olive	188-190	82	156	13.74 (14.02)	43.17 (43.02)	3.34 (3.16)	23.23 (23.12)
11	$[Cu(BNPAH_2)(ANP)_2]\ Cl_2$	Pale green	242-244	80	134	9.77 (9.94)	____	___	____

Elemental analysis(CHN)of ligand and some of the prepared complexes is a good agreement with that calculated for the proposed formula. Chloride determination ratio using direct titration (Moor method)[10]. The molar conductivities ΛM of the complexes in 10^{-3}M DMF at (25°C) (Table1) suggested 1:2 and non–electrolytes for complexes [11].These results are consistent with the given formulations. Comparison of the infrared spectral bonds of ligand and its complexes gives very useful information about the nature of the bonding as well as binding sites. The infrared spectrum of the ligand (Table-2) shows characteristic stretching absorption band at the region 1684 cm^{-1}as due to ν(C□ O)of carbonyl group[12].For the complexes, negative shifts 1632-1662$cm^{-1}$are observed in these bands due to coordination throw carbonyl oxygen atom [13]. The other band is located at 1591cm^{-1} due to ν(C□ N$)_{ring}$[14],which shifts towered lower frequency region 1530–1581cm^{-1}in case of all complexes, suggesting coordination through N atom of ν(C□ N$)_{ring}$ group[15]. The unaltered position of a band due to ν(N-H) of amide group in all the metal complexes indicates that, these groups are not involved in the coordination. Another band which appeared at 3238 cm^{-1}due to ν(NH_2) stretching[16], in the 2-amino-5-nitro pyridine(ANP) is shifted to the lower field 3204-3232 cm^{-1}in the adduct compounds. In addition of these changes, a new band prepares at 449-498$cm^{-1}$and 520-572cm^{-1}(not observed in the spectra of the free ligand) assigned to the stretching modes of M-N and M-O bands respectively [17]. For the ν(M-Cl) band of complexes could not be observed since it is located below the limits of our infrared spectrophotometer this becomes consistent with the molar conductivity measurements of these complexes and form the estimated amount of the chloride in the complexes[18].

Table-2: Important IR Spectra bands (cm-1) for BNPAH2 ligand and its complexes.

Compound	**□(C=N) ring**	**□(C=O)**	**□(M-N)**	**□(M-O)**
BNPAH$_2$ (L$_1$)	1591(m)	1684(m)	----	----
[Mn(BNPAH$_2$)Cl$_2$]	1569(m)	1632 (m)	494(w)	572 (s)
[Fe(BNPAH$_2$)Cl$_2$]	1568(m)	1630 (w)	465(s)	535(m)
[Co(BNPAH$_2$)Cl$_2$]	1568(m)	1632(m)	497(w)	544(m)
[Ni(BNPAH$_2$)Cl$_2$]	1581(w)	1641(w)	463(m)	520(S)
[Cu(BNPAH$_2$)Cl$_2$]	1566(s)	1639 (m)	497(m)	536 (m)
[Mn(BNPAH$_2$)(ANP) $_2$] Cl$_2$	1569(m)	1633 (w)	497(m)	536 (w)
[Fe(BNPAH$_2$)(ANP) $_2$] Cl$_2$	1570(m)	1643 (m)	449(s)	530(s)
[Co(BNPAH$_2$)(ANP) $_2$] Cl$_2$	1572(w)	1643 (m)	498(m)	559 (m)
[Ni(BNPAH$_2$)(ANP) $_2$] Cl$_2$	1569(w)	1640 (w)	472(s)	567 (w)
[Cu(BNPAH$_2$)(ANP) $_2$] Cl$_2$	1568(m)	1638 (s)	496(m)	544 (m)

s=strong, m=medium, w=weak

Table-3: Electronic spectral data (cm-1)and magnetic moment of the complexes.

No.	**Comple x**	**Absorption region (cm^{-1})**	**Possible assignment**	**μeff (BM)**
1	[Mn(BNPAH$_2$)Cl$_2$]	27778	C.T*	5.86
2	[Fe(BNPAH$_2$)Cl$_2$]	11338 34125	$^5T_{2g}$ □ ^5E_g C.T*	4.94
3	[Co(BNPAH$_2$)Cl$_2$]	12376 14970 18797 32467	$^4T_{1g}$ (F) □ $^4T_{2g}$ (F) □1 $^4T_{1g}$ (F) □ $^4A_{2g}$ (F) □2 $^4T_{1g}$ (F) □ $^4T_{1g}$ (P) □3 C.T*	4.50
4	[Ni(BNPAH$_2$)Cl$_2$]	10225 14577 25510 30120	$^3A_{2g}$ (F) □ $^3T_{2g}$ (F) □1 $^3A_{2g}$ (F) □ $^3T_{1g}$ (F) □2 $^3A_{2g}$ (F) □ $^3T_{1g}$ (P) □3 C.T*	2.92
5	[Cu(BNPAH$_2$)Cl$_2$]	10893 29586	^2E_g □ $^2T_{2g}$ C.T*	1.87

6	$[Mn(BNPAH_2)(ANP)_2]Cl_2$	34875	C.T*	5.97
7	$[Fe(BNPAH_2)(ANP)_2]Cl_2$	10870 33753	$^5T_{2g}$ □ ^5E_g C.T*	5.12
8	$[Co(BNPAH_2)(ANP)_2]Cl_2$	14836 26875	^2E_g □ $^2T_{2g}$ C.T*	1.89
9	$[Ni(BNPAH_2)(ANP)_2]Cl_2$	11494 14792 25000 32610	$^3A_{2g}$ (F) □$^3T_{2g}$ (F) □1 $^3A_{2g}$ (F) □$^3T_{1g}$ (F) □2 $^3A_{2g}$ (F) □$^3T_{1g}$ (P) □3 C.T*	3.12
10	$[Cu(BNPAH_2)(ANP)_2]Cl_2$	10163 35000	^2E_g □ $^2T_{2g}$ C.T*	1.84

(*) charge Transfer

The electronic spectra of Mn(II) complexes(1,6) showed that the d-d transitions, doubly forbidden from the fundamental term $^6A_{1g}$ towards, the quartet terms $^4T_{1g}$(G), $^4T_{2g}$(G) , $^4A_{1g}$, ^4E_g (G) exhibit a very small intensity and are concealed by the intra ligand transitions[19]. The absorption bands at, 27778, 34875 cm^{-1}can be attributed to the charge transfer of ligand to metal [20]. The complexes show magnetic moment in therange at 5.86,5.97 BM. Basing on this discussion a high spin octahedral arrangement may be proposed around Mn(II) ion[21].

The electronic spectra Fe (II) complexes(2,7) exhibited absorption bands at 10870,11338cm^{-1}which are caused by the electronic transition $^5T_{2g} \rightarrow {}^5E_g$[22] and another bands at 33753, 34125 cm^{-1}which belong to charge transfer[23]. The magnetic moment values of 4.94 ,5.12 BM supported a octahedral of the type high spin around Fe(II) ion[24].

The electronic spectrum of Co(II) complexes(3) displays absorptions at 12376, 14970, 18797cm^{-1}corresponding to $^4T_{1g}$ (F) → $^4T_{2g}$ (F)ν_1 , $^4T_{1g}$ (F) → $^4A_{2g}$ (F)ν_2 and $^4T_{1g}$ (F) → $^4T_{2g}$ (P) ν_3 respectively . The position of these bands is in true with prediction of high spin octahedral complex [25]. The magnetic moment of Co(II) complex exhibited magnetic moment value of 4.99 BM which is the high spin octahedral environment[26].The Co(II) complex(8)showed a band from d-d transition was observed at 14836 cm^{-1}which may be assigned to $^2E_g \rightarrow {}^2T_{2g}$ corresponding to a low spin octahedral environment around Co^{2+} ion[27].The magnetic moment of Co (II) complex was found to be 1.89 BM, which is at the lower end of magnetic moment expected for low spin octahedral Co(II) complex[28].

The electronic spectra of Nickel (II) complexes (4.9) showed three bands at 10225-11494, 14577-14792 and 25000-25510 cm^{-1}which were assigned to the $^3A_{2g}$ (F) → $^3T_{2g}$ (F)ν_1, $^3A_{2g}$ (F) → $^3T_{1g}$ (F)ν_2 and $^3A_{2g}$ (F) → $^3T_{1g}$(P)ν_3 transition respectively indicating octahedral geometry around Ni $^{2+}$ion[29]. The magnetic moment at values 2.92, 3.12 BM for the two complexes (4,9) confirmed the presence of two electrons with their octahedral environment[30].

The electronic spectrum of copper(II)complexes(5,10) showed abroad _ band at about 10163,10893 cm^{-1}attributed to $^2E_g \rightarrow {}^2T_{2g}$ transition [31]. This is indicative of distorted octahedral geometry for the Cu(II) complexes. The magnetic moment values of Cu (II) complexes (5,10) have been found to be 1.84 - 1.87 BM ,which is due to one unpaired electron. The data agrees well with the distorted octahedral geometry [32].

The ^{1}HNMR spectrum of the free ligand was recorded in DMSO_d^6. The ligand exhibited a signal at 5.55 ppm (2H)due to the alkene protons [33]. In the range of 6.50 ppm(4H) were assigned to chemical shifts for protons of methylene protons[34]. The NH proton of amide group exhibited signal at 8.90 ppm (2H). The peaks observed at range 7.60 – 8.90 ppm are assignable to the protons of aromatic rings as multiplied peaks [35].

CONCLUSION

From the above discussion of various physicochemical and spectral studies we concluded that the ligand ($BNPAH_2$) in all complexes coordinated as tetra coordination chelating ligand and the complex is octahedral ligand is used as stabilized for mononuclear metal complexes and according to the measurements and theoretical calculation, the Mn(II),Fe(II),Co(II) ,Ni(II), and Cu(II) complexes and adduct compounds have octahedral geometries around central metal ion.Fig.2 and Fig.3

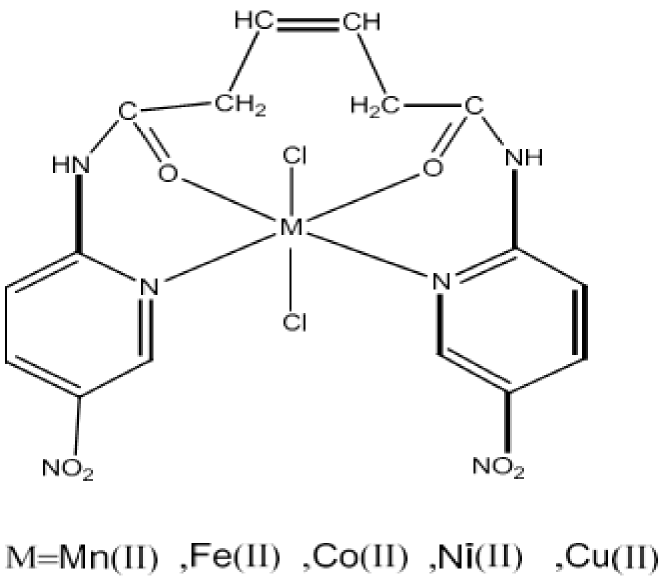

Fig 2: The Suggested Structures For ($BNPAH_2$) Complexes.

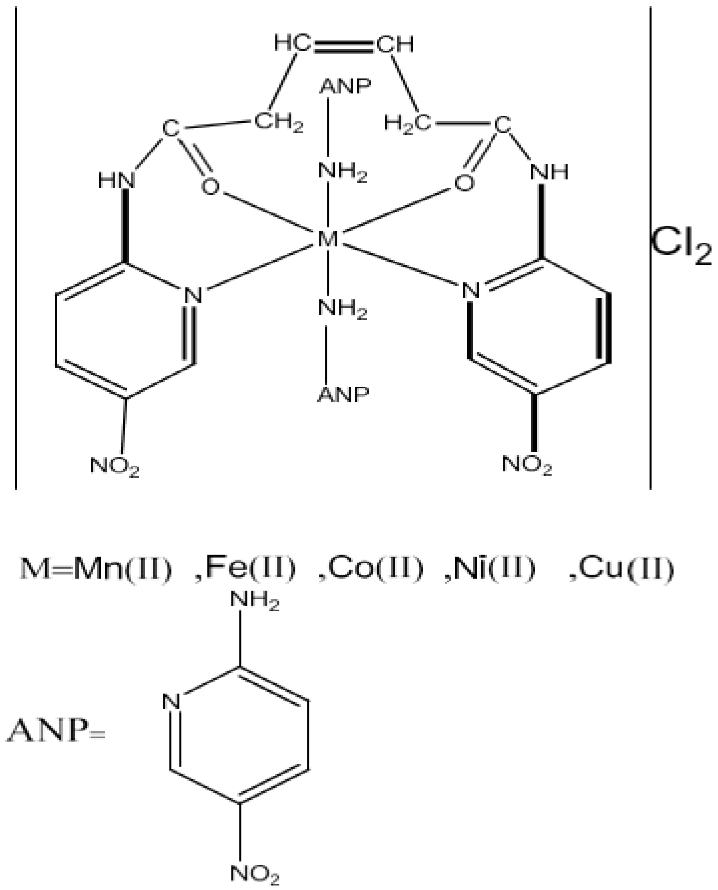

Fig 3: The Suggested Structures For (BNPAH2) Adducts Complexes.

REFERENCES

[1]. Kahovec.J, Kratochvil.P, Jenkins.A.D,Mita.I, Papisov.I.M, Sperling.L.H. and Stepto.R.F.T, (1968), Pure&Appl.Chem., pp 69(12),2511.
[2]. Faridbood .F, Ganjali .M.R, Dinarvand.R, Norouzi .P and Riahi .S , ,(2008)Sensors ,8,1645.
[3]. Black .D.S.C and Markham .E, (1965) ,Rev.PureAppl.Chem., 15,109.
[4]. Temel .H and Ilhan .S, (2008), Spectochim.Acta Part A. , 69 ,896.
[5]. Curtis .N.F (1968), Coordination Chem. Rev., 3, 3.
[6]. Peisach.J, Aisen.P and Blumberg .W,(1977),Eds.,"TheBiochemistry of Copper", Academic Press, New York, Adv. Chem. Ser., No. 100, (1971); No. 162.
[7]. Chaudhary .A, Jaroil .D.P. and Singh. R., (2002), Metal-Based Drugs, 8(6), 347.
[8]. Pomarnacka .E, Bednarski P.J, Grunert .R, Brzozowski .Z and Lach .J, (2006), Polish J.Chem., 80, 429.
[9]. Li .M.Y, Hu.P.Z, Zhu. W.R. and K.X.Xu , (2003), Chin.Chem.Lett. , 14(6), 572.
[10]. Vogel .A.I, (1989) "Vogel's Textbook of Quantitative analysis"5th Ed, Longman Scientific and Technical, England, 349,324-329.
[11]. Aliyu .H.N. and Galadima. A, (2009), Biosci.Res.Commun., 21,5.
[12]. Startton .W.J, (1970) ,Inorg.Chem., 9,517.
[13]. Srivastava .k.P, Singh .S.K and Mishra .B.P,(2014) Int.J.Chem.Tech. Res.,7(5)2272-2279.
[14]. Hua. T.X.Shi,Z.W and Hui. L.F,Chinese., (2013).J.Inorg.Chem, 29,1- 5.
[15]. Jayaseelan P,Prasad S,danayaki .S and Rajavel. R. Euro. ,(2011) ,J.Chem. 2(4), 480.
[16]. Nakanishi .K, (1964) "Infrared Absorption Spectroscopy-Practical",157.
[17]. Faruddin .M.A.A and Asafa .S, (2014) World, J.pharm. Res.,3(8), 467-480.
[18]. Pfirrmann .S, Limberg. C and Hoppe .E, (2009), Z.Anorg.Allg.Chem., 635, 312-316.
[19]. Kheiri .F. M. N, Tsipisand.C.A,Manoussakis G. E., (1977),Inorg. Chim. Acta. , 25,223.
[20]. Nicolls .D, (1984), "Complexes and First-row Transition Elements", Translated by W. Ibrahim College of scieuce University of Mosul , Iraq., pp.108, 229, 231, 235.
[21]. Chandra .S. and Gupta .L.K, (2005), Spectrochimica Acta Part A, 61, 2549.
[22]. Spinu .C, Pleniceann .M and Tigee .C, (2008),J.serb.Chem.Soc., 73(4) 415-421.
[23]. Ahmed.A.H, Omran.A.A and El-Sherbine.G.M, (2006),J.Appl. Sci.Res., 2(1), 44- 50.
[24]. Shakir .M , Mohamed .A.K, Varkey .S.P, Nasman.O.S.M. and Siddiqi.Z.A, (1995), Polyhedron , 14(10),1277.
[25]. Tayagi .M, Chandra .S, Akhtar .J and Chand .D, (2014), Spectrochim. Acta A, 118, 1056-1060.
[26]. Chandra .S and Gupta. K, (2002) , Trans.Met.Chem., 27,196.
[27]. Sallomi .I.J and Al-Fadhel .M.S, (1998), J,Ed.Sci. , 29, 5.
[28]. Holah .D.G and Murphy .C.N, (1972), Inorg.Nucl.Chem. Letters, 8, 1069.
[29]. Dwired .D.K, KShukla .R and Shukla. B.K, (1990) , Asian. J.Chem., 2,286.
[30]. Ibrahim.K.M, Bekheit.M.M., AbuEl-Reash.G.M and Mostafa.M.M ,(1986), Polyhedron, 5,1635.
[31]. Amaladasan .M and Victor Arockiadoss. P.,(2012),"International Jarnal of pharmaceutical sciences and Research" , 3(5),1327-1330.
[32]. Saha .N and Gayen.N.C, (1983), J.Indian.Chem.Soc., 60,317.
[33]. Hegazy .W.H and Gaafar. A.E, (2012) ,Am. Chem. Sci.J., 2(3) 86-99.
[34]. Faruddin .M.A.A. and Asafa .S, (2014), World,J. Pharm. Res., 3(8),467- 480.
[35]. Parshanthi .Y and Raj. S., (2010), J.Sci.Res., 2(1)114-126.