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Synthesis and Characterization of Some New Metals Complexes of [N-(4-Nitrobenzoyl Amino)-Thioxomethyl] Phenylalanine

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Abstract

A new ligand [N-(4-nitrobenzoylamino)-thioxomethyl] phenylalanine is synthesized by reaction of 4-nitrobenzoyl isothiocyanate with phenylalanine (1:1). It is characterized by micro elemental analysis (C.H.N.S.), FT-IR, (UV-Vis) and ^{1}H and ^{13}CNMR spectra. Some metals ions complexes of this ligand were prepared and characterized by FT-IR, UV-Visible spectra, conductivity measurements, magnetic susceptibility and atomic absorption. From results obtained, the following formula $[M(NBA)_2]$ where M^{2+} = Mn, Co, Ni, Cu, Zn, Pd, Cd and Hg, the proposed molecular structure for these complexes as tetrahedral geometry, except copper and palladium complexes are have square planer geometry.

Key words: Phenylalanine, 4-Nitrobenzoylisothiocyanate, Metal complexes.

Introduction

Amino acids are organic molecules containing amino group-NH_2 and carboxylic acid group-COOH, both attached to the same carbon atom called α-carbon,[1] aminoacids and their derivatives have been used for different purposes[2-3] and some amino acid derivatives and some of their metal complexes have been evaluated as having antibacterial, antifungal properties[4-6]. M.H. Salunke and Coworkers [7] were reported the synthesis and characterization of Schiff base derived from phenylalanine and its complexes, and also synthesis and characterization of new transition metal of phenyl alanine derivative[8].

The aim of this work is preparation some new metal ions complexes of [N-(4-Nitrobenzoyl Amino)-thioxomethyl] phenylalanine (NBA).

Materials and Methods:

(4-Nitrobenzoyl chloride), (Phenylalanine) (Fluka), Manganese chloride tetrahydrate ($MnCl_2.4H_2O$), Cobalt chloride hexahydrate ($CoCl_2.6H_2O$), Nickel chloride hexahydrate ($NiCl_2.6H_2O$), Copper chloride dehydrate ($CuCl_2.2H_2O$), Zinc chloride ($ZnCl_2$), Palladium chloride ($PdCl_2$), Cadmium chloride hydrate ($CdCl_2.H_2O$) and Mercury chloride ($HgCl_2$). All reagents were analar or chemical pure grade by BDH, Merck and Fluka.

Instruments

^{1}H and ^{13}C-NMR was recorded using Ultra Shield 300 MH_z Switzerland at University of Al al-Bayt, Jordan. Melting point was recorded by using Stuart- melting point apparatus. FT-IR spectra were recorded as KBr disc using 3800 Shimadzu in the range of 4000-400 cm^{-1}. Electronic spectra were obtained by using UV-160 Shimadzu spectra photometer at 25 ºC in (1x10^{-3}) M DMSO. Conductivity was measured by using Philips Pw. Digital. Micro elemental analyses (C.H.N.S) were performed by using acrlo Erba 1106 elemental analyzer. Magnetic susceptibility measurements were obtained by balance magnetic susceptibility by model MSB-MKI. Metal contents of the complexes were determined by atomic absorption technique by using Shimadzu (AA680G).

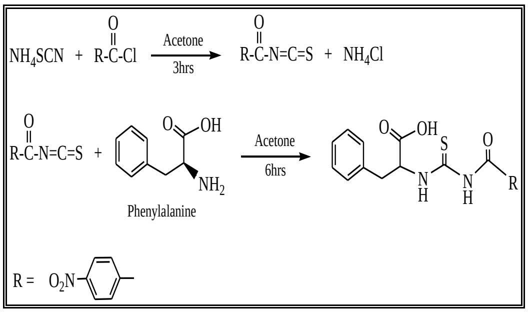
Preparation of (NBA)

1- Preparation of the (4-nitrobenzoyl isothiocyanate)

Mixture of 4-nitrobenzoyl chloride (4.34g, 1mmol) and ammonium thiocyanate (2g, 1mmol) in (25ml) of acetone was stirred under refluxed for 3 hours and then filtered, the filtrate was used for further reaction [9].

2- Preparation of[N-(nitrobenzoylamino)thioxomethyl] phenylalanine (NBA)

(4.84g, 1mmol) of phenylalanine in (20ml) acetone was rapidly added to the maintain vigorous reflux. After refluxing for 6 hours, the resulting solid was collected, washed with acetone and recrystallization from ethanol. Scheme (1),Yield (82%), (m.p =178-180) ºC, C% found (54.63) while calculate (54.69), H% found (4.12) while calculate (4.02), N% found (11.36) while calculate (11.26), S% found (8.88) while calculate (8.58).



Scheme (1): Preparation of (NBA)

Synthesis of metal complexes

(0.75g, 2mmole) of (NBA) was dissolved in 25ml of ethanol containing (0.12g, 2mmole) of KOH, then the solution of following metal salts $MnCl_2.4H_2O$ (0.2g, 1mmole), $CoCl_2.6H_2O$ (0.24g, 1mmole), $NiCl_2.6H_2O$ (0.24g, 1mmole), $CuCl_2.2H_2O$ (0.2g, 1mmole), $ZnCl_2$ (0.14g, 1mmole), $PdCl_2$ (0.2g, 1mmole), $CdCl_2.H_2O$ (0.2g,1mmole), and $HgCl_2$ (0.3g,1mmole) in ethanol, were added dropwise to the solution of (NBA^-K^+). The precipitate formed immediately after stirring the mixture at room temperature for 3hours. The precipitate was collected by filtration, washed with distilled water and ethanol and dried under vacuum. Physical properties were given in Table (1).

Results and Discussion

The solid complexes were soluble in some common solvent such as dimethyl formamide, dimethyl sulphoxide, and relatively thermally stable. The molar conductivity of all complexes in DMSO were found to be non-electrolyte, Table (1) includes the physical properties for (NBA) and its metal complexes.

Table (1): Physical properties of (NBA) and its metal complexes

Compund	M.wt (gm/mol)	Color	M.p °C or dec.	M% Calculation (Found)	Molar condu. Ohm^{-1}Cm^{2}mol^{-1}	μ_{eff} (B.M)
(NBA)	373	Yellow	178-180	-	8	-
[Mn(NBA)$_2$]	798.9	Pale yellow	140-142	6.87 (6.44)	7.2	5.97
[Co(NBA)$_2$]	802.93	Green	146-148	7.34 (7.56)	4.9	4.92
[Ni(NBA)$_2$]	802.71	Pale green	136-138	7.31 (7.35)	20	3.02
[Cu(NBA)$_2$]	807.54	Pale green	138-140	7.86 (8.21)	8.8	1.77
[Zn(NBA)$_2$]	809.37	Yellow	143-145	8.07 (7.52)	18	0
[Pd(NBA)$_2$]	951.2	Brown	134-136	21.78 (21.68)	8.2	0
[Cd(NBA)$_2$]	856.4	Pale yellow	130-132	13.12 (12.85)	9.2	0
[Hg(NBA)$_2$]	944.59	Pale yellow	150 dec.	21.23 (20.86)	14.2	0

Spectral studies

^{1}H and ^{13}C-NMR spectra

1) ^{1}H-NMR spectrum for (NBA) in DMSO as solvent, Fig. (1) showed the following signals: doubled at δ(1.1) ppm for (2H, CH_2), singlet at δ(2.3) ppm for DMSO, quartet at δ(2.84-3.17) ppm for (1H, CH), singlet at δ(4.84-4.86) ppm for (1H,NH sec.amine), multiplet at δ(6.97-8.33) ppm for (aromatic protons), singlet at δ(8.52) ppm for (1H, NH sec.amide), singlet at δ(10.82-10.87) ppm for (1H, COOH)[10].

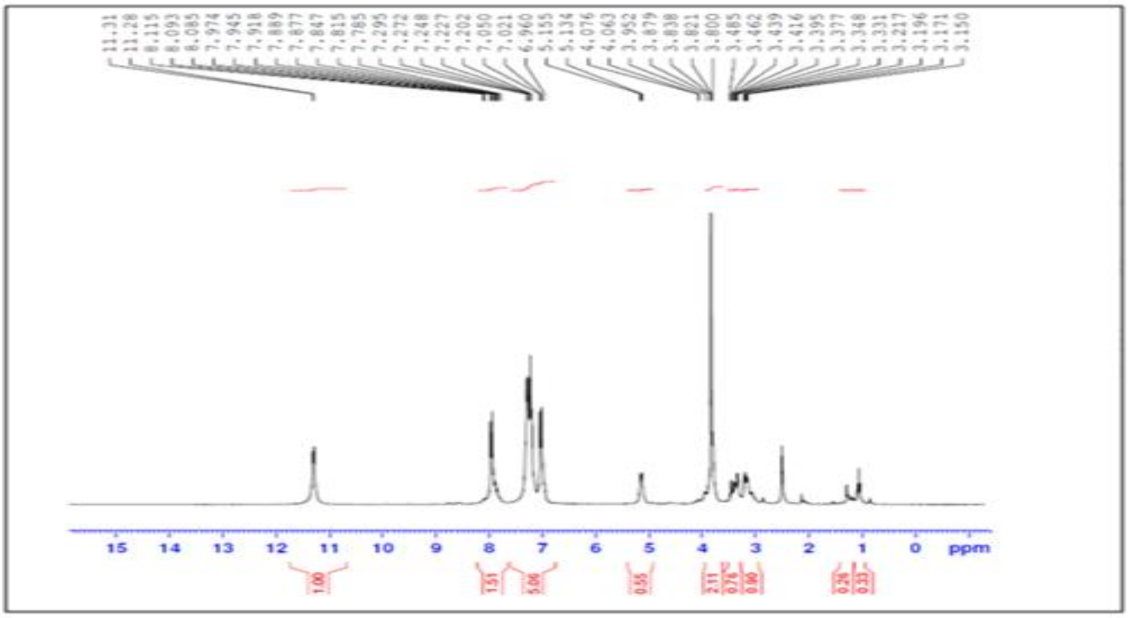


Fig. (1): ^{1}HNMR spectrum of (NBA)

2) The ^{13}C-NMR spectrum for (NBA) in DMSO, Fig. (2) showed the following signals: signals at δ(36.51) ppm for (CH_2), signals at δ(38.69-40.37) ppm for DMSO, signal at δ(58.98) ppm for (CH), signals at δ(108.01-166.76) ppm for aromatic carbons, signal at δ(170.21) ppm for (C=O sec.amide), signal at δ(171.28) ppm for (COOH), signal at δ(179.57) ppm for (C=S).

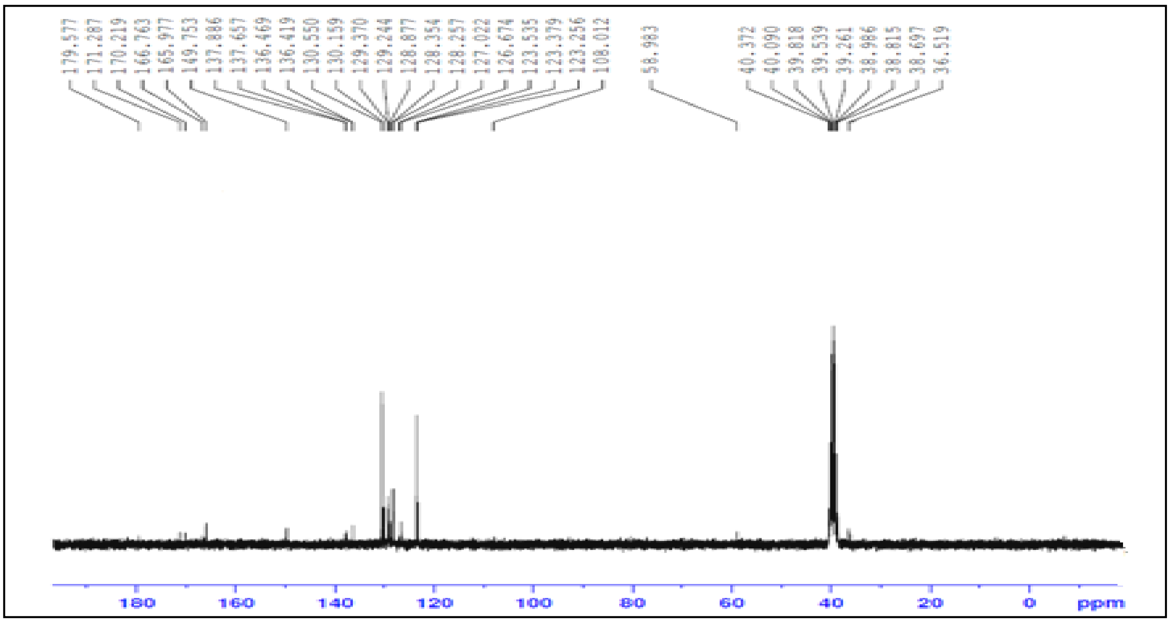


Fig. (2): ^{13}CNMR spectrum of (NBA)

Infrared spectra

FT-IR spectrum of the free (NBA), Fig. (3), showed bands due to amido υ(NH), υ(C=O) and υ(C=S) which absorbed at (3412) cm^{-1}, (1606) cm^{-1}, and (1288) cm^{-1} respectively, while another absorption band appeared at (1666) cm^{-1} could be explained as υ$(COO)_{asym}$[11] [12], where the υ$(OCO)_{sym}$ was noticed at (1413) cm^{-1}. The FT-IR spectra of complexes exhibited marked difference between bands belonging to the stretching vibration of υ(NH) of the amine group in the range between (3328-3294) cm^{-1} shifted lower frequencies by (14-118) cm^{-1} suggesting of the possibility of the coordination of (NBA) through the nitrogen atom at the amine group[13]. Absorption assigned for υ$(COO)_{asym}$ was noticed at the range (1624-1523) cm^{-1} shifted to higher frequencies by (42-143) cm^{-1} while the band caused by υ$(COO)_{sym}$ appeared between (1523-1446) cm^{-1} shifted to lower frequencies by (110-33) cm^{-1} which indicates to the coordination of the carboxylic group to the central ion[14]. The stretching vibration band υ(C=O) and υ(C=S) carbonyl group either shows no change or very little in their frequencies (1600-1604) cm^{-1} and (1280-1253) cm^{-1} respectively there for indicating do not coordinate to the metal ion[15]. Metal- nitrogen and metal-oxygen bonds were confirmed by the presence of the stretching vibration of υ(M-O) and υ(M-N) around (405-435) cm^{-1} and (470-423) cm^{-1} respectively. Table (2) describes the important bands and assignment for free (NBA) and its complexes. The FTIR spectrum of Mn complex showed in Fig. (4).

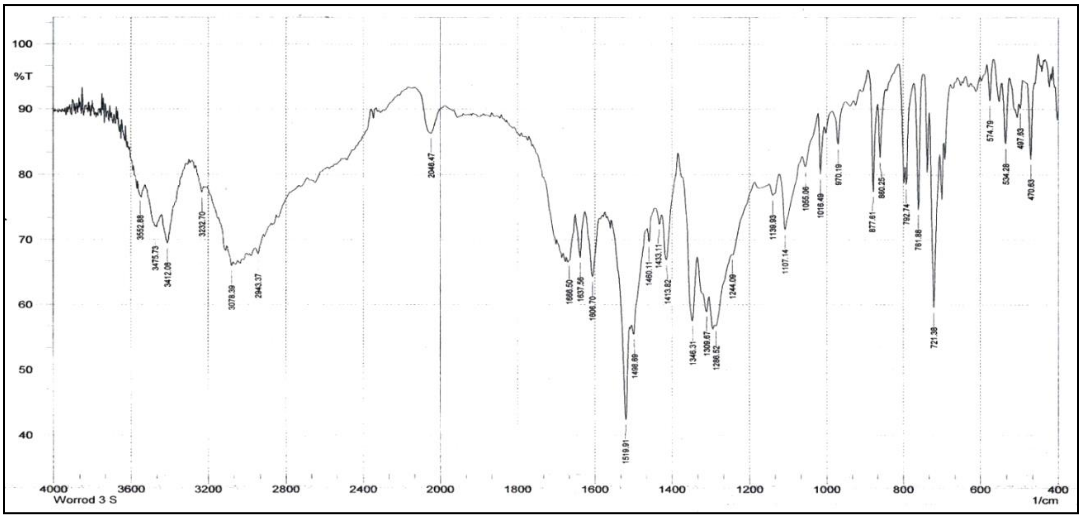


Fig. (3): FT-IR spectrum of (NBA)

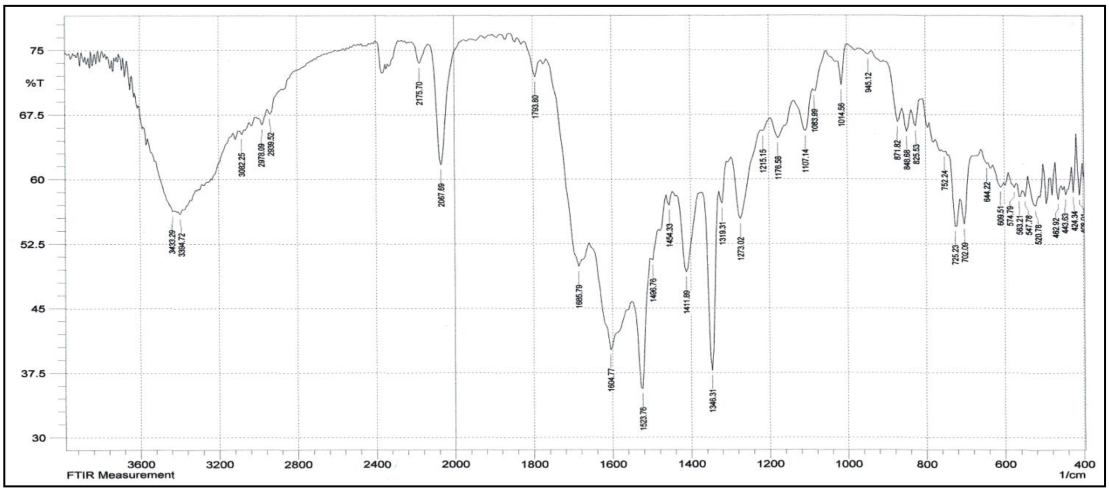


Fig. (4): FT-IR spectrum of [Mn(NBA)$_2$]

Table (2): Some FT-IR frequencies in (cm^{-1}) for (NBA) and its metal complexes

Compound	υ(N-H)	υ(COO)$_{sym}$	υ(COO)$_{asym}$	υ(C=O)	υ (C=S)	υ(M-O)	υ (M─N)
(NBA)	3412 (m)	1413 (s)	1666 (m)	1606 (s)	1288 (s)	-	-
[Mn(NBA)$_2$]	3394 (m)	1454 (s)	1523 (m)	1604 (w)	1273 (s)	424 (m)	443 (w)
[Co(NBA)$_2$]	3398 (m)	1473 (m)	1527 (s)	1604 (m)	1280 (s)	408 (m)	443 (w)
[Ni(NBA)$_2$]	3394 (b)	1523 (m)	1577 (m)	1600 (m)	1276 (s)	432 (w)	462 (w)
[Cu(NBA)$_2$]	3398 (b)	1523 (m)	1624 (m)	1600 (m)	1273 (s)	424 (m)	466 (w)
[Zn(NBA)$_2$]	3392 (m)	1523 (m)	1589 (s)	1600 (m)	1276 (s)	428 (w)	443 (m)
[Pd(NBA)$_2$]	3394 (b)	1453 (w)	1523 (s)	1600 (m)	1276 (s)	432 (w)	470 (w)
[Cd(NBA)$_2$]	3398 (b)	1523 (s)	1566 (m)	1600 (w)	1276 (m)	405 (m)	435 (m)
[Hg(NBA)$_2$]	3294 (b)	1446 (m)	1543 (s)	1600 (m)	1253 (s)	435 (m)	493 (m)

b = browed, w = weak, s = strong, m = medium

Electronic spectral

The UV-Visible spectra of (NBA) and its complexes recorded in Table (3), the solution of (NBA) in 10^{-3}M (DMSO) exhibited two peaks Fig. (5) at (33557) cm^{-1} and (26246) cm^{-1} which are attributed to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transition respectively[16].

The spectra of complexes

[Mn(NBA)$_2$] d^5: The pale yellow complex of Mn (II) shows band at (33670) cm^{-1} due to charge transfer and another bands at (13642) cm^{-1} and (11737) cm^{-1} which are caused by the electronic transfer $^6A_1\rightarrow{}^4T_{1(G)}$ and $^6A_1\rightarrow{}^4T_{2(G)}$ respectively[17].

[Co(NBA)$_2$] d^7: The spectrum of the blue-green complex gave three bands at, (33898) cm^{-1},(25974)cm^{-1}, (21052) cm^{-1} and (12437) cm^{-1} attributed to (C.T), $^4A_2\rightarrow{}^4T_{1(P)}$, $^4A_2\rightarrow{}^4T_{1(F)}$ and $^4A_2\rightarrow{}^4T_{2(F)}$ respectively, and the rach interelectronic repulsion parameter (B^-) was found to be (647.6) cm^{-1}, from the relation $\beta=B^- / B_0$, was found to be a equal (0.67), these parameter are accepted to Co(II) tetrahedral complex[18].

[Ni(NBA)$_2$] d^8: The spectrum of deep green complex of Ni (II) has revealed the following electronic transfer (C.T), $^3T_{1(F)}\rightarrow{}^3T_{1(P)}$, $^3T_{1(F)}\rightarrow{}^3A_{2(F)}$ and $^3T_1\rightarrow{}^3T_{2(F)}$, transition at (33670) cm^{-1}, (26666) cm^{-1}, (20408) cm^{-1} and (11376) cm^{-1} respectively, the (B^-) value found to be (863) cm^{-1}, while β was equal to (0.83) these are the characteristics for tetrahedral complexes of Ni (II)[19].

[Cu(NBA)$_2$] d^9: The spectrum of brown complex of Cu(II) Fig. (6) show three bands at (33670) cm^{-1}, (13351) cm^{-1} and (11750) cm^{-1} caused to (C.T), $^2B_{1g}\rightarrow{}^2A_{1g}$ and $^2B_{1g}\rightarrow{}^2B_{2g}$ transition respectively[20].

[Pd(NBA)$_2$] d^8: The spectrum of brown complex of Pd(II) gave three bands at (33670) cm^{-1}, (28985) cm^{-1} and (13661) cm^{-1} attributed to (C.T), $^1A_{1g}\rightarrow{}^1B_{1g}$, $^1A_{1g}\rightarrow{}^1A_{2g}$ transition respectively[18].

The complexes of **[Zn(NBA)$_2$]**, **[Cd(NBA)$_2$]** and **[Hg(NBA)$_2$]** shows only charge transfer of (M→L) at (33670) cm^{-1}, (33444) cm^{-1} and (33557) cm^{-1} respectively[21]. All transition with their assignments are summarized in Table (3).

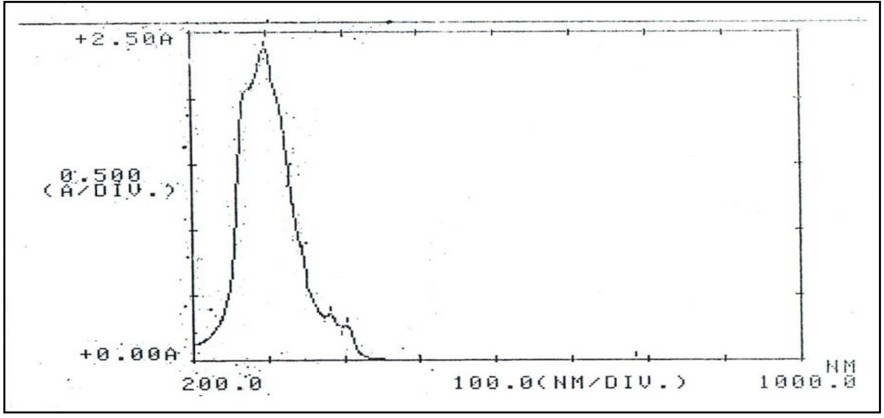


Fig. (5): Electronic spectrum of (NBA)

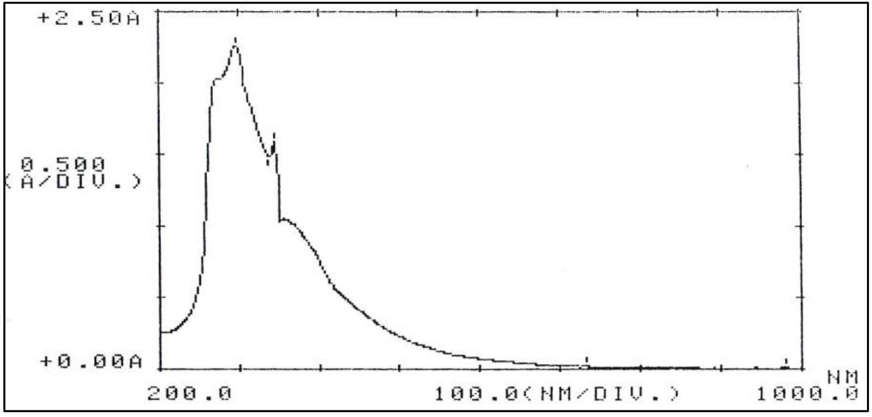


Fig. (6): Electronic spectrum of [Pd(NBA)$_2$]

Table (3): The peaks electronic transitions and structure geometries of (NBA) and its complexes

Compound	λ (nm)	ύ (cm^{-1})	ABC	$ε_{max}$	Transition
(NBA)	298	33557	2.211	2211	$\pi \rightarrow \pi^*$
	381	26246	0.140	140	$n \rightarrow \pi^*$
$[Mn(NBA)_2]$	297	33670	2.224	2224	C.T
	733	13642	0.018	18	$^6A_1 \rightarrow {}^4T_{1(G)}$
	852	11737	0.016	16	$^6A_1 \rightarrow {}^4T_{2(G)}$
$[Co(NBA)_2]$	295	33898	1.282	1282	C.T
	385	25974	0.890	890	$^4A_{2(F)} \rightarrow {}^4T_{1(P)}$
	475	21052	0.030	30	$^4A_{2(F)} \rightarrow {}^4T_{1(F)}$
	804	12437	0.016	16	$^4A_{2(F)} \rightarrow {}^4T_{2(F)}$
$[Ni(NBA)_2]$	297	33670	2.213	2213	C.T
	375	26666	0.910	910	$^3T_{1(F)} \rightarrow {}^3T_{1(P)}$
	490	20408	0.025	25	$^3T_{1(F)} \rightarrow {}^3A_{2(F)}$
	879	11376	0.010	10	$^3T_{1(F)} \rightarrow {}^3T_{2(F)}$
$[Cu(NBA)_2]$	297	33670	2.315	2315	C.T
	749	13351	0.014	14	$^2B_{1g} \rightarrow {}^2A_{1g}$
	851	11750	0.010	10	$^2B_{1g} \rightarrow {}^2B_{2g}$
$[Zn(NBA)_2]$	297	33670	2.248	2248	C.T
$[Cd(NBA)_2]$	299	33444	2.304	2304	C.T
$[Hg(NBA)_2]$	298	33557	2.301	2301	C.T
$[Pd(NBA)_2]$	297	33670	2.258	2258	C.T
	345	28985	1.589	1589	$^1A_1 \rightarrow {}^1B_{1g}$
	732	13661	0.050	50	$^1A_{1g} \rightarrow {}^1A_{2g}$

C.T = Charge transfer

According to spectral data as well as those obtained from elemental analyses, the chemical structure of the complexes may be suggested as tetrahedral for $[M(NBA)_2]$ where M^{2+} = (Mn, Co, Ni, Zn, Cd and Hg), Fig. (7) while Copper and Palladium complexes have square planer.

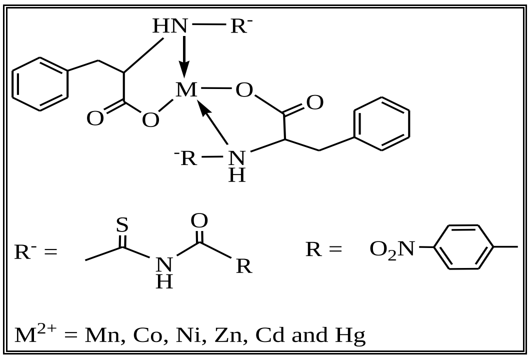


Fig. (7): Suggested structure of complexes $[M(NBA)_2]$

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تحضير وتشخيص بعض المعقدات الفلزية الجديدة مع [N- (4- نايتروبنزويل امينو- ثايواوكسومثيل)] فنيل الانين

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الخلاصه:

حضر الليكاند الجديد [N- (4- نايتروبنزويل امينو- ثايواوكسومثيل)] فنيل الانين من تفاعل (4- نايتروبنزويل ايزوثايوسيانات) مع فنيل الانين وبنسبة (1:1) الذي شخص بوساطة التحليل الدقيق للعناصر (كاربون، هيدروجين، نتروجين، كبريت)، وأطياف كل من الاشعة تحت الحمراء والاشعة فوق البنفسجية - المرئية والرنين النووي المغناطسي للبروتون والكاربون. حضرت بعض معقدات الليكاند وشخصت بأطياف الاشعة تحت الحمراء والفوق بنفسجية - المرئية وقياسات التوصيلية والحساسية المغناطيسية والامتصاص الذري .واعطت النتائج الصيغة العامة $[M(NBA)_2]$ حيث M^{2+} = منغنيز، وكوبلت، ونيكل، ونحاس، وخارصين، وبلاديوم، وكادميوم وزئبق، كانت نتائج التشخيص ان التراكيب الجزيئية للمعقدات ذات شكل رباعية السطوح، عدا معقدي النحاس والبلاديوم ذات شكل مربع مستوي.

الكلمات المفتاحية : فنيل الانين، 4- نايتروبنزويل ايزوثايوسيانيت، المعقدات الفلزية.