ISSN: 0975 -8542

Journal of Global Pharma Technology

Available Online at: www.jgpt.co.in

RESEARCH ARTICLE

Synthesis and Spectroscopic Study of 3-Hydroxy-2-(3-(4-Nitrobenzoyl) Thiouriedo) Propanoic Acid with their Metal Complexes

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Abstract

A new ligand 3-hydroxy-2-(3-(4-nitrobenzoyl) thiouriedo) propanoic acid (NTP) where synthesized by reaction of 4-nitro benzoyl isothiocyanate with serine amino acid. The ligand was characterized by FT-IR, NMR spectra and the elemental analysis. The transition metal complexes of this ligand where synthesize and characterized by UV-Visible spectra, FT-IR, magnetic suscpility, conductively measurement, The general formula [M (NTP) $_2$] where M^{+2}= (Mn, Co, Ni, Cu, Zn, Cd, Hg,), the form of molecular for these complexes as tetrahedral except Cu has square planer.

Keywords: *Serine, 4-nitrobenzoyl isothiocyanate, Transition metals.*

Introduction

Amino acids play an important role in cell building, tissue repair and the synthesis of antibodies that resist various types of bacteria and viruses and interfere in the manufacture of many compounds such as hormones, enzymes and pigments. It also represents the intermediate state of cellular metabolism [1]. Serine is a class of neutral or unbalanced polar amino acids. The lateral group (R) of the hydroxyl group is composed of the methyl group CH_2, a non-essential amino acid that is synthesized within the body and is a source.

To store glucose in the liver and muscles and works to strengthen the immune system by filling the need for antibodies, and works to create the outer envelope of lipid acid located around the nervefibres [2,3] many of serine derivatives were synthesized by different methods, Alicia Boto and coworkers, are prepare series of serine derivatives, like: Methyl (Acetyloxy) (benzoylamino) acetate, Methyl 2-Benzamido-2-(2-oxooxazolidin-3-yl) acetate and Methyl2-Benzamido-2-(3,5-dioxo-4-phenyl-1,2,4-triazolidin-1-yl)acetate [4], and also (4-toluenesulfonyl-L-serine) [5] ,and also Mohammad Hakimi and coworkers synthesized some of copper complexes with serine and its derivatives like the complexes [D-Serine-L-serine-copper (II)] [6], [D,L:L,D-(2-Amino-3-hydroxypropanoato)-(2aminobutanoato)-copper(II)] [7] , and [(D)-2-Amino-3-hydroxypropanoato)-((L)-2-amino butanoato)-copper(II)] [8].

Experimental

Chemicals

Metal salts ($MnCl_2.4H_2O$, $CoCl_2.6H_2O$, $NiCl_2.6H_2O$, $CuCl_2.2H_2O$, $CdCl_2.H_2O$, ZnCl2 and $HgCl_2$) were obtained from fluka, Merck, serine amino acid, 4-nitrobenzoyl chloride and ammonium thiocyanate (Fluka).

Instrumentations

^{1}H NMR was recorded using Ultra Shield 300 MHz Switzerland ,at university of Al al-Bayt, Jordan, melting point was recorded by using stuat-Melting point apparatus, FTIR spectra were recorded by KBr discs using 3800 shimadzu at the range (4000-400)cm^{-1}. Electronic spectra were obtained using UV-160 shimadzu spectrophotometer at 25°C in 10^{-3}M DMSO. Conductivity was measured by using Philips pw. Digital .Elemental analyses C.H.N.S were performed using a Carlo 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).

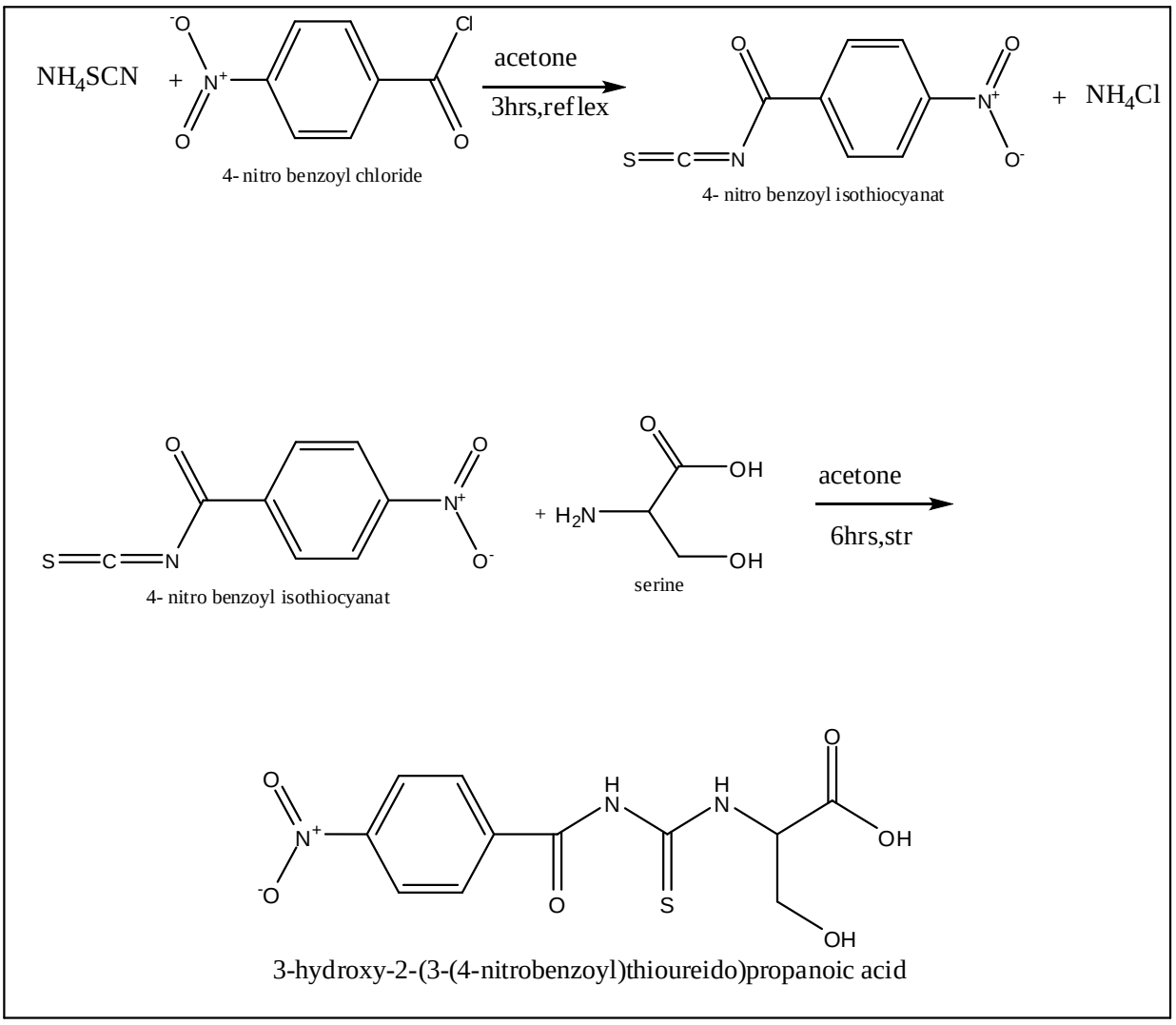
Preparation of the ligand (NTP)

Preparation of the 4-nitro benzoyl isothiocyanate [7]

dissolve (4.82g,26Mmole) of 4-nitro benzoyl Chloride in 15 ml of acetone and (2gm,26Mmole)of ammonium thiocyanate in 25ml acetone and mixed them, stirring for 3hours and then filtered, the filtrate was used for further reaction.

Preparation of 3-hydroxy-2-(3-(4-nitrobenzoyl) thiouriedo) propanoic Acid

Dissolved(2.77g,26Mmole)of the amino acid (serine) in 15 ml acetone and added the former solution to it ,then reflex and stirring the mixture for 6 hours, The resulting solid was collected, washed with acetone and recrystallized from ethanol(m.p=148-150)°C, yield=80% scheme(1) %C found (42.47) while calc. 42.17 %H found (3.144) while calculate(3.51), %N found (13.77) while calculate (13.41) and %S found (10.115) while calculate (10.22). This yields agreement with the suggested formula ($C_{11}H_{11}N_3O_6S$).



Scheme1: Synthesis route for the preparation ligand (NTP)

Preparation of the Complexes

(0.626g, 2Mmole) of the ligand (NTP) was dissolved in (25ml) of ethanol containing (0.112g,2Mmole) of KOH. a solution(5ml) of (1mmole) metal salte ($MnCl_2$. $4H_2O$, $ZnCl_2$, Co $Cl_2.6H_2O$, $NiCl_2.6H_2O$, $CuCl_2$. $2H_2O$, Cd $Cl_2.H_2O$ and $HgCl_2$) (0.2g, 0.136g, 0.237g, 0.237g, 0.170g, 0.201g and 0.272g) respectively.

In ethanol(10ml) was added drop wise to the mixture, and the precipitate formed

immediately, after stirring the mixture at room temperature for 3 hours, the precipitate was collected by filtration, washed with water- ethanol and dried.

Results and Discussion

The molar conductivity of the ligand (NTP) with some their metal complexes in DMSO solvent, are shown in Table (1) the values of molar conductivity, indicates the non electrolyte behavior of these complexes.

Spectral Studies

The (NMR) Spectra (NTP)

^{1}H-NMR Spectrum

The (^{1}H, NMR) spectrum of the ligand (NTP) shown in Figure (2) showed the following signals:

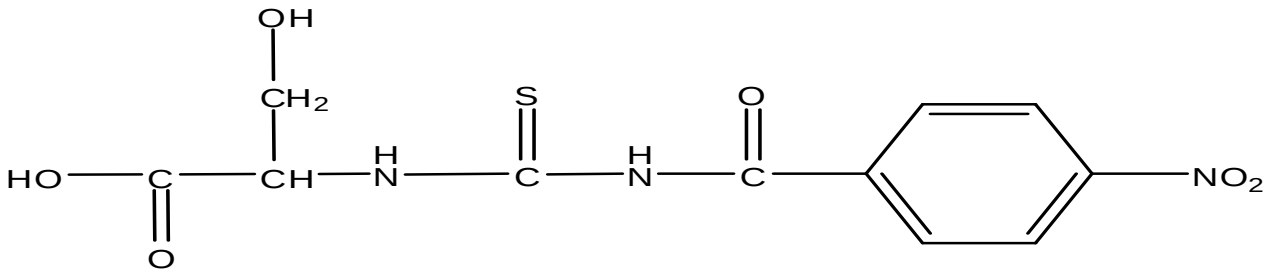


Fig 1: the ligand (NTP)

Malty signals du to DMSO solvent between δ(2.098-2.509)ppm, spectrum showed triplet signal at δ(1.549)ppm for (1H,CH),and doublet signal at δ(3.430)ppm to (2H.CH_2),singlet signal at δ(4.912)ppm for (1H,OH),so singlet at δ(7.680)ppm du to (1H,$NH_{thiourea}$), singlet at δ(8.082)ppm du to (1H,NH_{amid}), a doublet signal at δ(8.111-8.364) ppm for (4H,$_{aromatic}$), and singlet sginal at (11.287)ppm for (1H,COOH). The Table (2) showed the signals chemical shifting by ppm for (NTP).

(^{13}CNMR) Spectrum (NTP)

The spectrum (^{13}CNMR) for the ligand (NTP) Fig (3) showed the following signals:

The spectra showed signals between δ (38.690-40.356)ppm for solvent di methyl selfoxid (DMSO),and a singlet signal at δ(59.490)ppm for (CH_2),and other signal at δ(60.400)ppm to (CH),and malty signals between δ(123.296-149.804)ppm for(4C,$_{aromatic}$), singlet peak at δ(166.168)ppm du to (C=O $_{sec\ amide}$), and singlet peak at δ(170.582)ppm for (COOH),and single peak at δ(179.981) for (C=S). The Table (3) showed the signals chemical shift by ppm for (NTP).

Infrared Spectra

The characteristic vibrations of ligand (NTP) and their complexes as KBr disc are described in Table (4). The spectrum of free ligand (NTP) Fig (4) exhibited medium band at (3417) cm^{-1} this could be attributed to υ (N-H), While the other medium band at (3178) cm^{-1} du to (OH). Other band at(1728)cm^{-1}, which belong to $\upsilon(COO)_{asym}$ and (1346)$cm^{-1}$for $\nu(COO)_{sym}$,a strong band at ν(1670)cm^{-1}du to ν(C=O)group, υ(C=S)were found at(1257)cm^{-1} [9, 10].

The FT-IR spectra of the prepared complexes exhibited υ (N-H) in the range of (3460-3417) cm^{-1} which shows a shifted to the higher frequencies in compared with free ligand suggested. The possibility of the coordination of ligand through the nitrogen atom at the amine group [11, 12].Absorption assigned for $\upsilon(COO)_{sym}$ was noticed at the range (1400-1419) cm^{-1} shifted to higher frequencies by (54-73) cm^{-1}.

While the band caused by $\upsilon(COO)_{asym}$ appeared between(1624-1604)cm^{-1} Shifted to lower frequencies by(104-124)cm^{-1} which indicates the attach carboxylic group to the central metal ion[13, 14]. The stretching vibration bands υ(C=S) and υ(C=O) carbonyl group either show no change or very little in their frequencies therefore indicating do not coordinate to the metal ion [15].

Metal-nitrogen and metal-oxygen bands where confirmed by the presence of the stretching vibration of υ(M-O) and υ(M-N) in the range (520-423)cm^{-1} and (486-432)cm^{-1} respectively. Fig (5) shows the FT-IR spectrum for the complex [Co (NTP) $_2$].

Magnetic Properties for the Metal Complexes

The magnetic moment (μ_{eff}) for complexes of $Mn^{+2}(d^5)$, and $Co^{+2}(d^7)$ were found to be (5.88) B.M, and (4.53) B.M respectively, which within the expected spin-only values [16].The higher value of μeff of the $Ni^{+2}(d^8)$ complex (3.11) B.M due to the orbital contribution [17, 18]. The magnetic moment μeff of the $Cu^{+2}(d^9)$ complex was found to be (1.71) B.M which within the expected value to one electron [19], All the data are shown in Table (1).

The Electronic Spectra

The spectrum of ligand (NTP) Fig (5) show bands at (36363) cm^{-1} and (26455) cm^{-1} which are attributed to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ respectively [20].

[Mn(NTP)$_2$] Complex

The yellow complex of Mn(II) shows band at (36496)cm^{-1}, which belongs to ligand-field and another band at (28735)cm^{-1} which is du to charge transfer ,the last band at(13227) caused by the electronic transition $^6A_1 \rightarrow {}^4T_{2(G)}$ [21].

[Co ((NTP) $_2$] Complex

The black-green complex of Co(II) shows four bands Fig(6),at (36101)cm^{-1}, (27027)cm^{-1},(14285)cm^{-1} and(10928)cm^{-1} which attributed to ligand-faild,

$^4A_{2(f)} \xrightarrow{v_3} {}^4T_{1(p)}$ mixed with(C.T), $^4A_{2(F)} \xrightarrow{v_2} {}^4T_{1(F)}$ and $^4A_2 \rightarrow {}^4T_{2(F)}$ transition respectively, and the rich inter electronic repulsion parameter B$^-$ was found to be (568.5)cm^{-1} from the relation(ß=B⁄Bo), ß was found to be equal(0.586). These parameters are accepted to Co (II) tetrahedral complex [22, 23].

[Ni (NTP) $_2$] complex

The electronic spectrum of green-yellow complex of Ni(II) has shown four bands at (36630)cm^{-1}, (28409)cm^{-1} , (13327)cm^{-1} and(10752)cm^{-1} revealed the following electronic transition; ligand-failed, $^3T_{1(F)} \rightarrow {}^3T_{1(P)}$ with C.T, $^3T_{1(F)} \rightarrow {}^3A_{2(F)}$ and $^3T_{1(F)} \rightarrow {}^3T_{2(F)}$ respectively. The B$^-$ value found to be (625) cm^{-1} while ß was equal to 0.60, these are the characteristics for tetra hedral complexes of Ni (II) [24, 25].

[Cu (NTP) $_2$] Complex

The spectrum of green-yellow complex of Cu (II) shows two bands at (36900) cm^{-1} and (12106) cm^{-1} which du to the ligand-field and $^2B_1 g \longrightarrow {}^2A_1 g$ [26].

[Zn (NTP) $_2$]

The orang complex of Zn (II) shows two bands at (36231) cm^{-1} and (28901) cm^{-1} are du to electronic transition the ligand-field and charge transfer respectively.

[Cd (NTP) $_2$]

The spectrum of deep-yellow complex of Cd (II) showed one absorptions band at (36231) cm^{-1} du to ligand field.

[Hg (NTP) $_2$]

The yellow complex showed one absorptions band at (36900) cm^{-1} du to ligand field, All transitions with their assignments are summarized in Table (6).

Table 1: Some physical properties of the ligand (NTP) and their metal complexes

Compound	M.wt (gm/mole)	Color	M.P(C) or dec.	M% Calculation (Found)	Molar Cond. $Ohm^{-1} cm^2 mol^{-1}$ in DMSO	μ_{eff} (B.M)
$C_{11}H_{11}N_3O_6S$ (NTP)	313	Dark-yellow	148-150	-	0.420	-
$[Mn(NTP)_2]$	678.9	Yellow	144	8.02 (8.45)	6.42	5.88
$[Co(NTP)_2]$	682.9	Black-green	290(dec)	8.62 (8.73)	5.00	4.53
$[Ni(NTP)_2]$	682.7	Green-yellow	107	8.59 (8.39)	4.53	3.11
$[Cu(NTP)_2]$	687.5	Green-yellow	162	9.23 (9.21)	4.56	1.71
$[Zn(NTP)_2]$	689.4	Orang	103	9.48 (9.65)	6.06	0

[Cd(NTP) $_2$]	736.4	Deep-yellow	210	15.26 (15.73)	5.10	0
[Hg(NTP) $_2$]	824.6	Yellow	215 (dec)	24.32 (---)	5.40	0

Table 2:1HNMR and chemical shift by ppm for (NTP)

Compound	Functional group	δ (ppm)
ANP	t(1H,CH)	1.549
	d(2H,CH_2)	3.480
	S(1H,OH)	4.912
	S (1H,NH amine)	7.680
	S(1H,NH sec amide)	8.082
	(d-d)(4H,aromatic proton)	(8.111-8.364)
	S(1H,COOH)	11.287

Table 3: the ^{13}CNMR in DMSO solvent chemical shift by ppm

Compound	Functional group	δ (ppm)
ANP	S (C,CH_2)	59.490
	S (C,CH)	60.400
	M (C, aromatic)	(123.296-149.804)
	S (C=O sec amine)	166.168
	S (COOH)	170.582
	S (C=S)	179.981

Table 4: shows the IR absorption values by cm^{-1} unit of (NTP) with its complexes

compound	υ(Coo) asym	υ(Coo) sym	Δ υ	υ(NH) υ(OH)	υ(C=S)	υ(C=O)	υ(MN)	υ(MO)
NTP	1728(S)	1346(S)	----	3417(M) 3178(M)	1257(M)	1670(S)	---	---
[Mn(NTP)$_2$]	1624(S)	1411(S)	213	3433(b)	1280(M)	1662(M)	466(W)	423(M)
[Co(NTP)$_2$]	1604(M)	1411(M)	193	3417(b)	1276(M)	1666(M)	470(M)	487(M)
[Ni(NTP)$_2$]	1608(M)	1419(S)	189	3425(b)	1275(M)	1627(M)	443(M)	475(M)
[Cu(NTP)$_2$]	1604(M)	1418(M)	186	3458(b)	1261(M)	1676(M)	447(M)	482(M)
[Zn(NTP)$_2$]	1604(M)	1408(M)	196	3417(b)	1280(M)	1662(M)	432(M)	489(M)
[Cd(NTP)$_2$]	1620(M)	1400(M)	220	3425(b)	1265(M)	1631(M)	455(b)	482(M)
[Hg(NTP)$_2$]	1604(M)	1415(M)	189	3460(b)	1276(M)	1678(M)	486(M)	520(M)

Table 5: Electronic spectral data of ligand (NTP) and its complexes in DMSO solvent

Compounds	λ(nm)	υ·(cm^{-1})	A	ε_{max} molar^{-1} cm^{-1}	Type of Transitions
NTP	275 378	36363 26455	2.082 0.500	2082 500	**π → π*** **n → π***
[Mn(NTP)$_2$]	274 348 756	36496 28735 13227	1.993 0.686 0.014	1993 686 14	L.F C.T $^6A_1 \rightarrow {}^4T_{2\,(G)}$
[Co (NTP)$_2$]	277 370 700 915	36101 27027 14285 10928	2.302 0.780 0.018 0.015	2302 780 18 15	L.F C.T * $^4A_{2\,(F)} \rightarrow {}^4T_{1\,(P)}$ $^4A_{2\,(F)} \rightarrow {}^4T_{1(F)}$ $^4A_{2\,(F)} \rightarrow {}^4T_{2\,(F)}$
[Ni(NTP)$_2$]	273 352 756 930	36630 28409 13227 10752	2.199 0.765 0.020 0.015	2199 765 20 15	L.F C.T $_{MIX}$ $^3T_1 \rightarrow {}^3T_{1\,(P)}$ $^3T_1 \rightarrow {}^3A_{2\,(F)}$ $^3T_1 \rightarrow {}^3T_{2\,(F)}$
[Cu(NTP)$_2$]	271 826	36900 12106	1.538 0.017	1538 17	L.F $^2B_1g \rightarrow {}^2A_1g$
[Zn (NTP)$_2$]	276	36231	2.272	2272	L.F

	346	28901	0.097	97	C.T
$[Cd(NTP)_2]$	276	36231	2.227	2227	L.F
$[Hg(NTP)_2]$	271	36900	1.734	1734	L.F

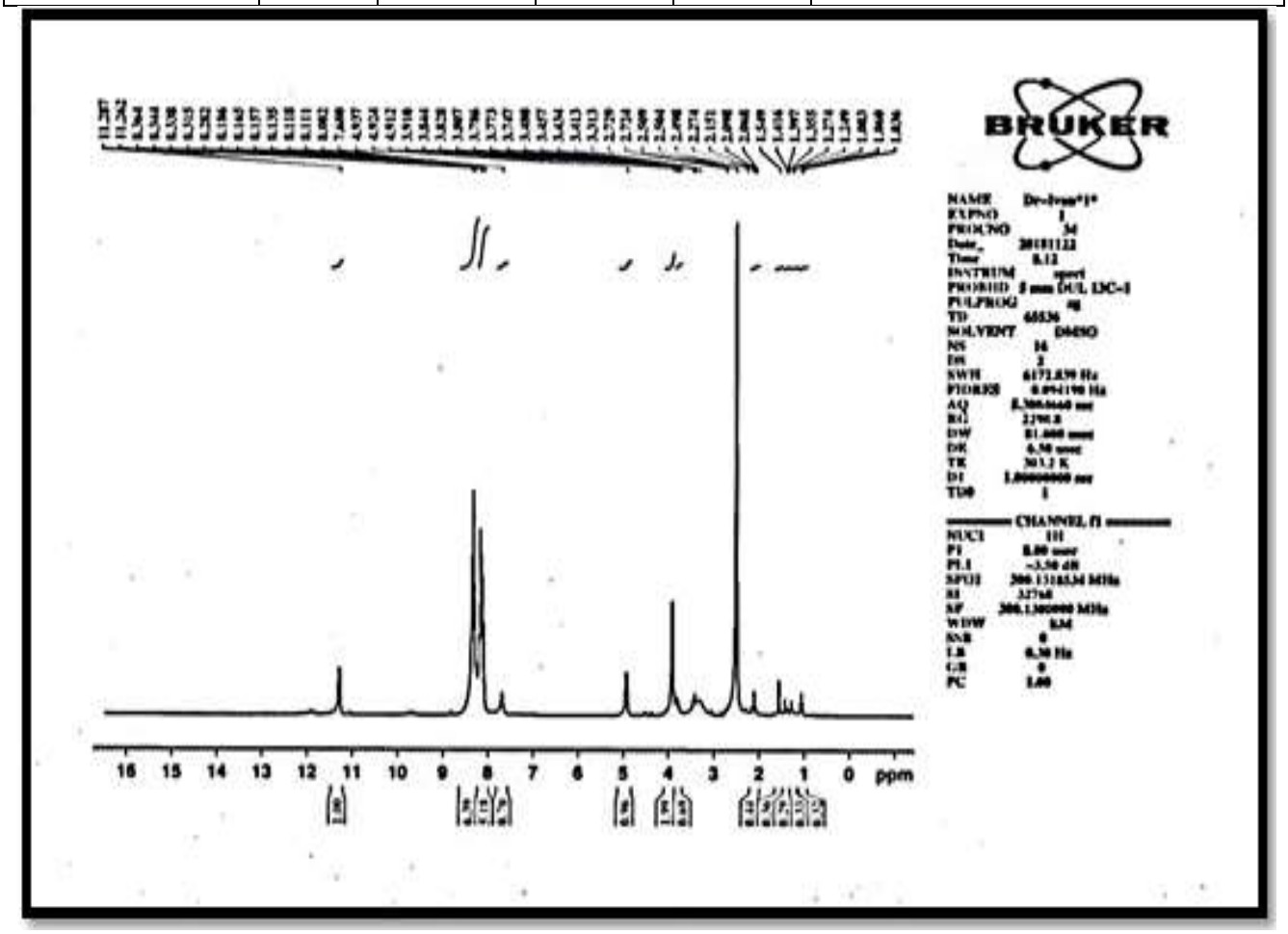


Fig 2: ^{1}HNMR spectrum of the ligand (NTP)

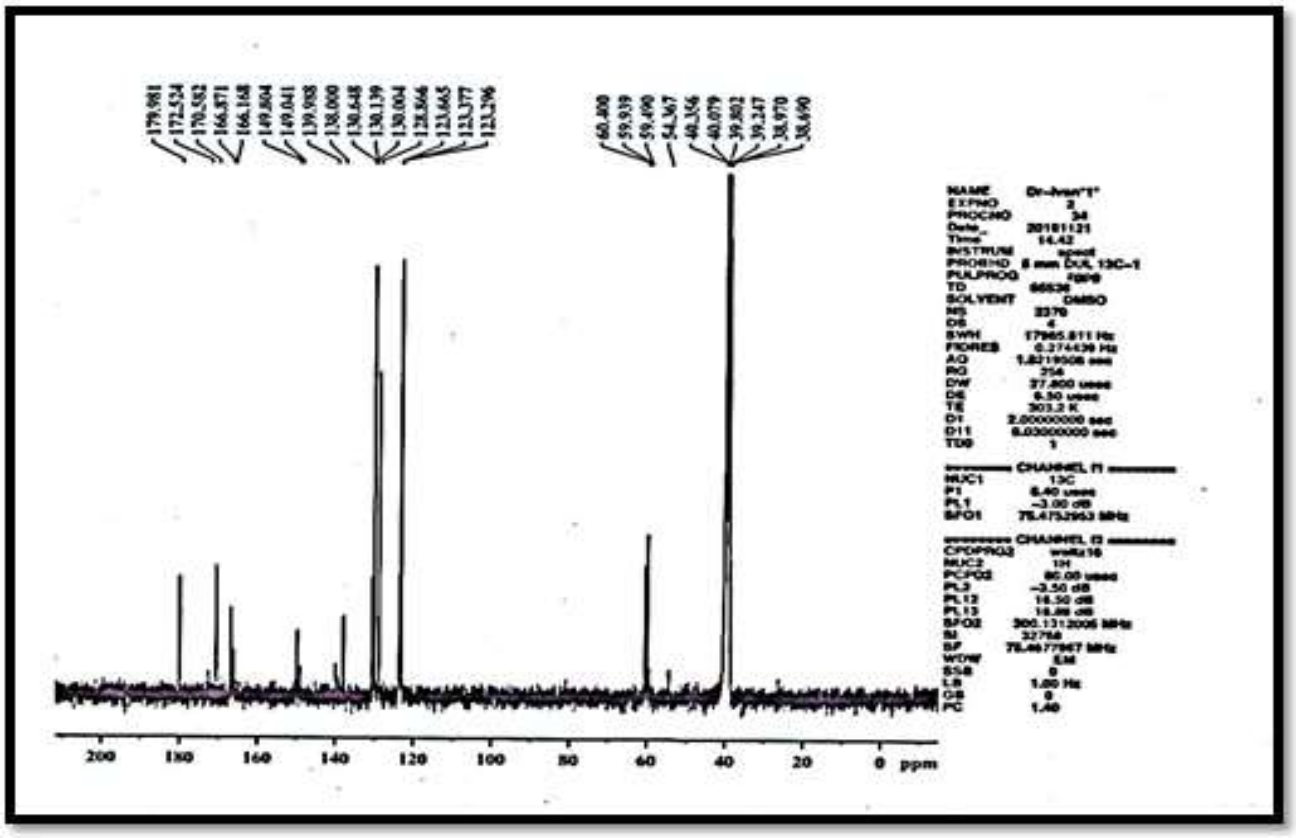


Fig 3: ^{13}C-NMR spectrum of the ligand (NTP)

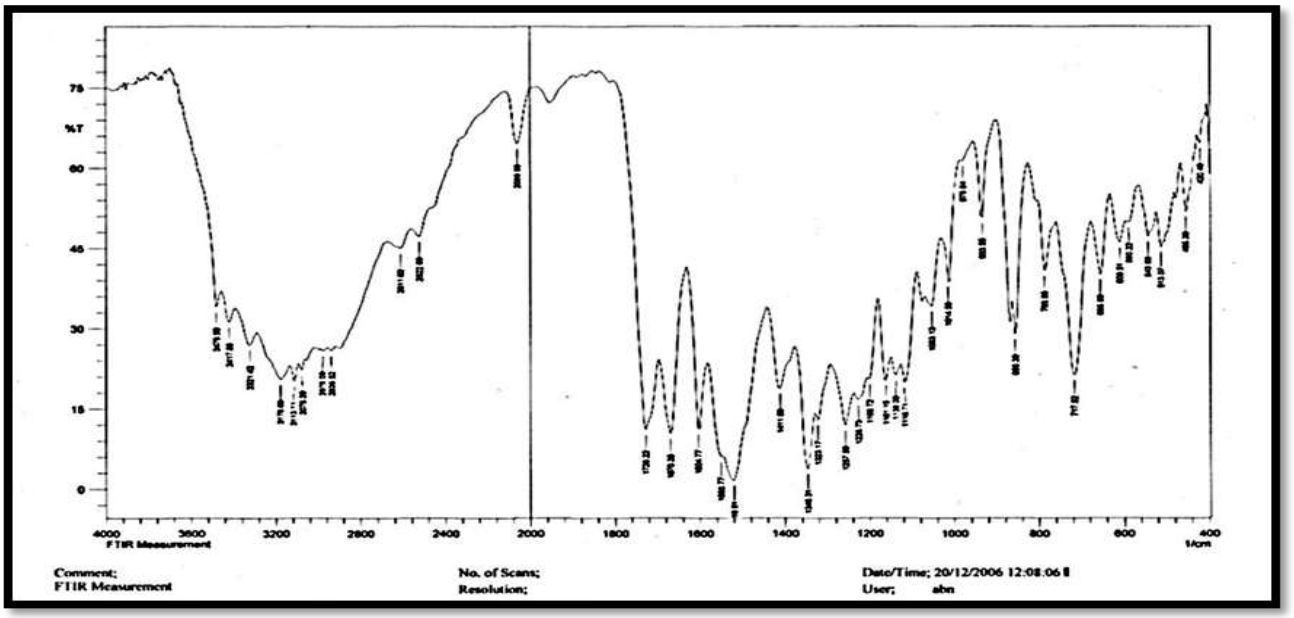


Fig 4: the FT-IR spectrum of the ligand (NTP)

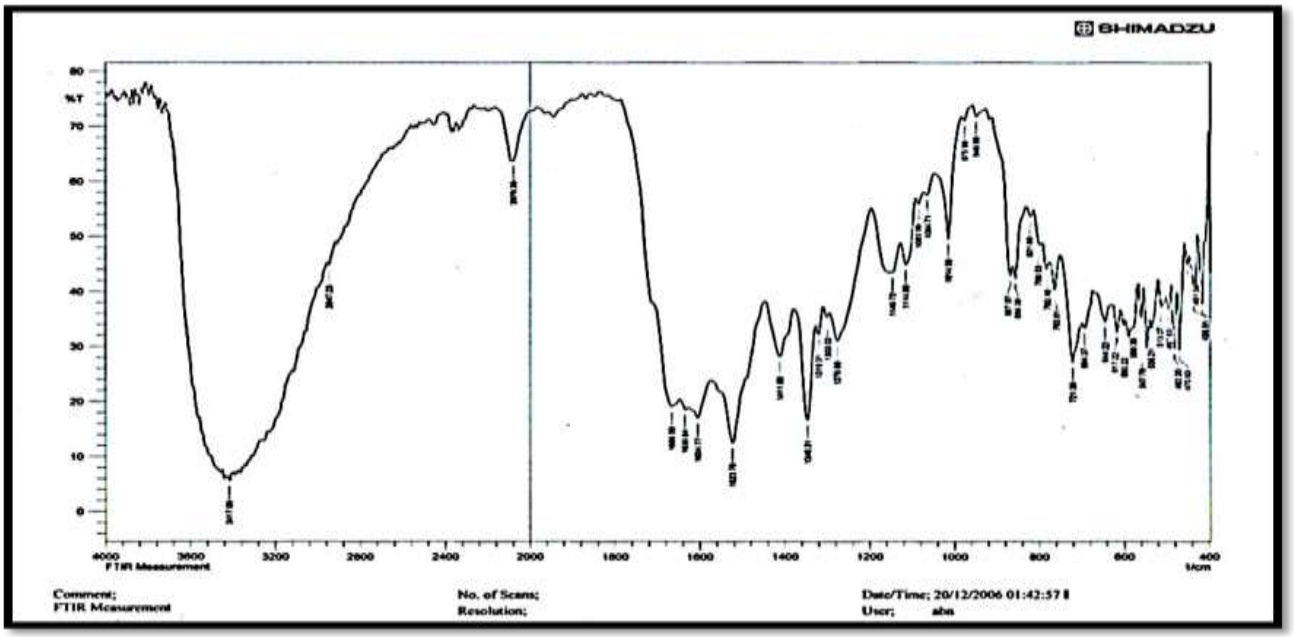


Fig 5: FT-IR spectrum for complex [Co (NTP) $_2$]

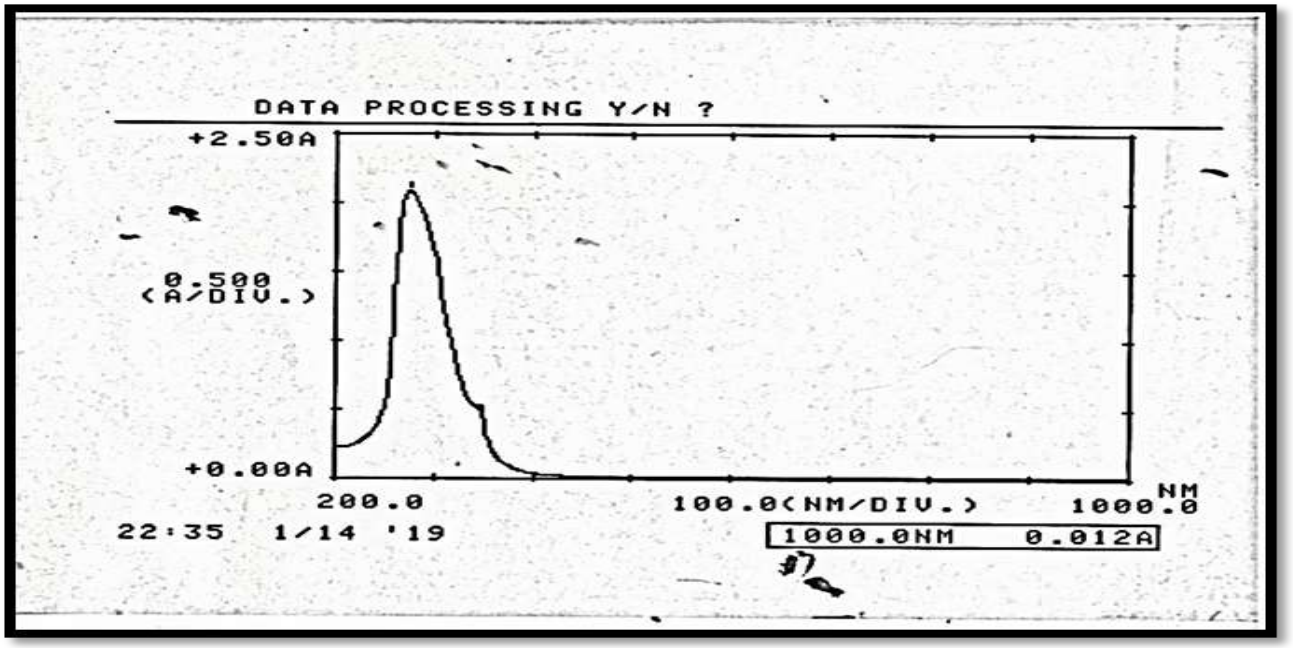


Fig 6: UV-visible spectrum for the ligand (NTP)

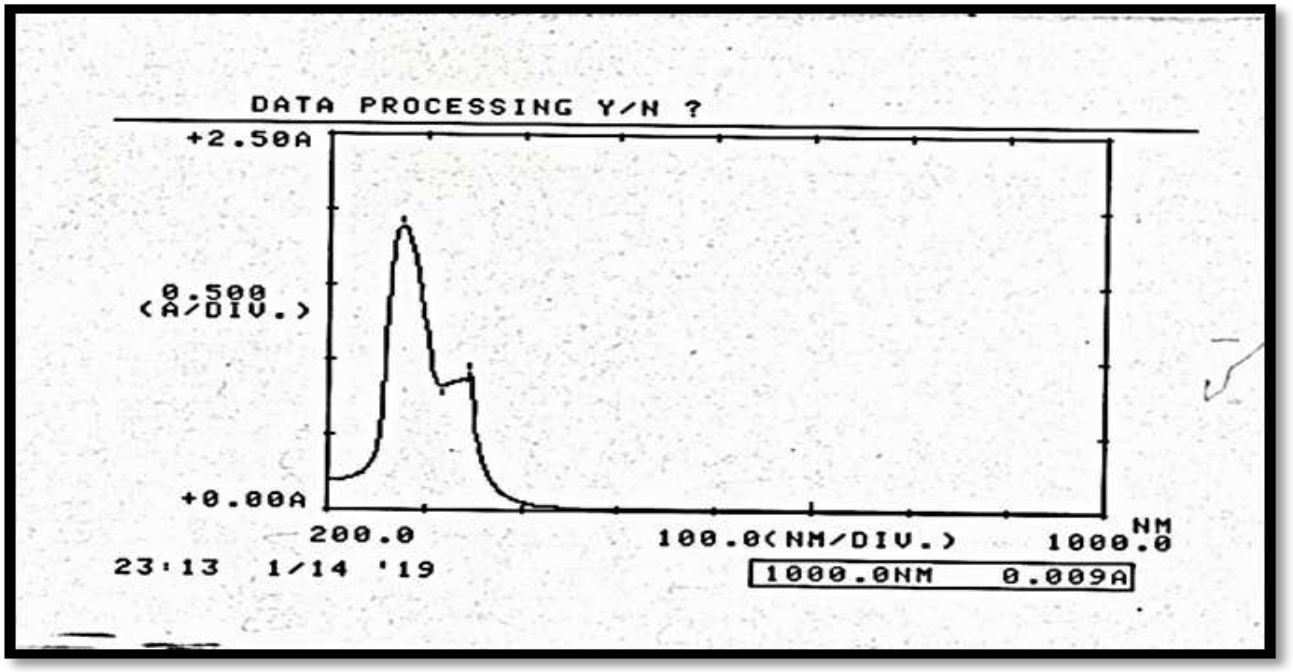
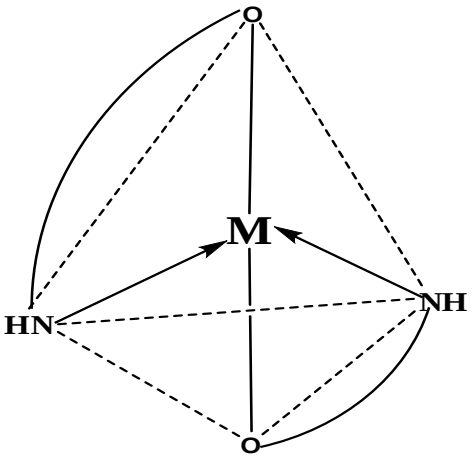


Fig 7: UV-visible spectrum of the complex [Zn (NTP) $_2$]

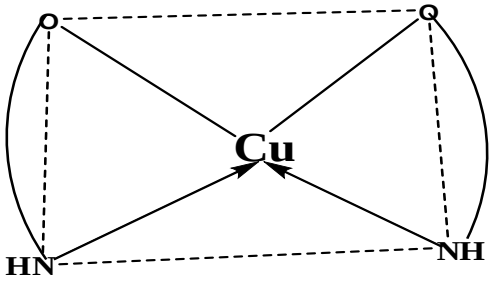
Conclusion

New I ligand in this work I have been prepared by reaction from 4-nitro benzoyl isothiocyanate I with I serine the ligand I was characterized by elemental Imicro analysis C.H.N.SI, IFT-IRI, IUV-Vis I and I1H, 13C-NMRI spectra.

The metal complexes of this ligand were prepared and characterized by FT-IR, UV-VisI spectra, conductivity I measurements, magnetic I susceptibility I and I atomic I absorption, the I proposed I geometrical I structure I for complexes were tetrahedral I geometry except copper complex has square planer, Scheme (2)show this geometry.

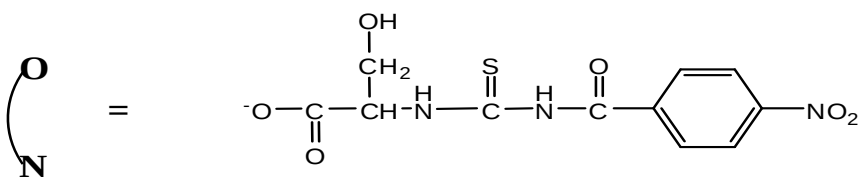


T.h



S.P

M= (Mn^{+2},Co^{+2},Ni^{+2},Zn^{+2},Cd^{+2},Hg^{+2})



Scheme2: general suggested geometry of the complexes [M (NTP) $_2$]

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