



Preparation and Characterization of novel metal complexes containing hydrazone derived from camphor and 2,4-dinitrophenyl hydrazine

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Abstract

Ligand The development of 2,4-dinitrophenyl hydrazine with camphor under demonstrated conditions yielded another hydrazone ligand. The structures of metal (II) for example, copper, nickel, cobalt, zinc and iron with hydrazone have been composed from reacting between copper bromide, nickel chloride hexahydrate, cobalt chloride hexahydrate, zinc chloride, and iron bromide with hydrazone in 1:2 molar ratio. The ligand and their metal complexes have been detached in a solid state. The spectroscopic data of the structures propose their 1:2 structures which are broke down by CHN, FT-IR and ¹H NMR spectroscopy. From spectroscopic reviews I proposed the octahedral structure for the all structures and the outcomes are spoken to and talked about underneath.

Keywords: 2,4-dinitrophenyl hydrazine, Complexes, hydrazone, metal complexes, camphor.

Introduction

Hydrazone subsidiaries have pulled in a lot of enthusiasm for manufactured science and extensive research on them in connection to their engineered utility has been expert. Hydrazones are widely considered as reactants or response intermediates since they can promptly experience different ring conclusion reactions¹. Hydrazones, RR-C=N-NR'R", are utilized as intermediates as a part of union², as practical gatherings in metal carbonyls³, in natural compounds^{4,5}, hydrazones display physiological exercises in the treatment of a few sicknesses, for example, tuberculosis. This movement is ascribed to the arrangement of stable chelate buildings with move metals which catalyze physiological processes⁶⁻⁸. They likewise go about as herbicides, bug sprays, nematocides, rodenticides, plant development controllers, sterilants for houseflies, among other applications^{6,7,9}. In logical science hydrazones discover applications as multidentate ligands for move metals in colorimetric or fluorimetric determinations^{10,11}. I report here the blend and portrayal of hydrazone Schiff base mixes. as of late the N-N linkage has been utilized as a key basic theme in different bioactive operators. Specifically, an expanding number of N-N bond-containing heterocycles and peptidomimetics have advanced into business applications as pharmaceutical and horticultural agents^{12,13}. The hydrazones have been exhibited to have antibacterial¹⁴⁻²⁰. Anticonvulsant²¹⁻²⁴. What's more, antitubercular activities²²⁻²⁸.

Materials and methods

Materials and Equipment: All reagents were of analytical grade from Merck, Fluka, Sigma-Aldrich or and BDH and used without further purification. ¹H NMR spectra was recorded on

Bruker 300 MHz spectrometers with TMS as an inward reference using DMSO-d₆ dissolvable. Infra-red spectra were recorded with KBr plates using a FTIR spectrophotometer Shimadzu show 8400 S in range 4000-400 cm⁻¹. Normal examination for Carbon, Hydrogen and Nitrogen were performed by using a Euro vector EA 3000A Elemental Analysis (Italy). Dissolving motivations behind each and every solid compound were settled using a MPS10 electrically warmed melting point mechanical get together. Produced pathways are presented in Schemes 1-2 and physicochemical, apparition data for the as of late joined blends are given in Tables-1 and 2.

Preparation of (E)-1-(2,4-dinitrophenyl)-2-(1,7,7-trimethyl bicyclo [2.2.1] heptan-2-ylidene)hydrazine: To 2,4-dinitrophenyl hydrazine (0.01 mol) in ethanol (20 mL), camphor (0.01 mol) was included. The response blend was warmed under reflux for 4 h then poured onto a measuring glass containing an ice/water blend. The framed strong item was gathered by filtration and dried to give orange gems (from ethanol). Yield: 89 %, m.p. 188 - 189°C.

Preparation of transition metal complexes: The main products in all reactions were synthesis by this method: the ligand of (E)- 1-(2,4-dinitrophenyl)- 2-(1,7,7-trimethylbicyclo [2. 2. 1] heptan-2-ylidene) hydrazine (0. 001 mol) was dissolved in (10 ml) of hot ethanol solution and mixed with CuBr₂, NiCl₂.6H₂O, CoCl₂.6H₂O, ZnCl₂ or FeBr₂ (0. 0005 mol) in (10 ml) of ethanol in mole ratio 1:2. The mixture was refluxed for 3 hrs. The mixture was cool at room temperature and the precipitated complex was then filtered off and dried. Then, the precipitate was recrystallized from methanol, Those

investigative What's more physical majority of the data of the edifices need aid recorded done Table-1.

Results and discussion

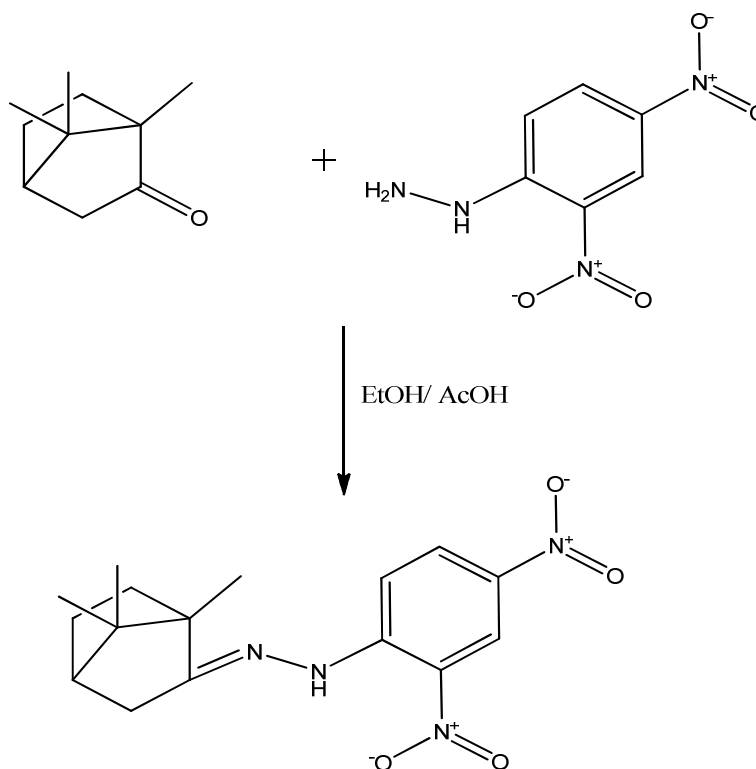
The compound (E)- 1-(2,4-dinitrophenyl)- 2-(1,7,7-trimethylbicyclo [2.2.1] heptan-2-ylidene)hydrazine is shaped in

great yield by the reacting of 2,4-dinitrophenyl hydrazine with camphor. Basic scientific information (Table-1) of the mixes recommend that the response between 2,4-dinitrophenyl hydrazine and camphor happened in the 1:1 proportion as in Scheme-1. Also, the instrument of hydrazone arrangement response as Scheme-2²⁸.

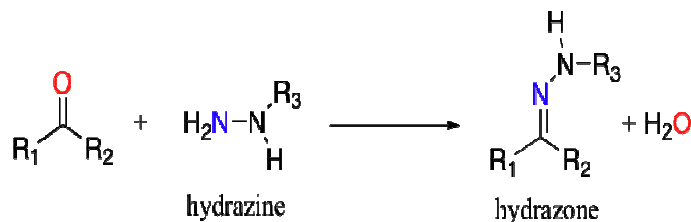
Table-1: Analytical and physical data for new ligand and their complexes 1-5.

Compounds	colour	Melting point (°C)	Analysis (%) ^a			Yield %
			C	H	N	
Ligand (L)	Orange	188 – 189	57.82 (57.55)	6.07 (6.01)	16.86 (16.45)	89
Cu(L) ₂ (H ₂ O) ₂ [1]	Reddish-brown	181 – 183	50.42 (50.31)	5.55 (5.46)	14.70 (14.75)	81
Fe(L) ₂ (H ₂ O) ₂ [2]	Brown	152 – 153	50.94 (50.70)	5.61 (5.35)	14.85 (14.38)	78
Zn(L) ₂ (H ₂ O) ₂ [3]	Orange	171 – 173	50.30 (50.22)	5.54 (5.43)	14.66 (14.81)	76
Ni(L) ₂ (H ₂ O) ₂ [4]	Orange	191 – 192	50.74 (50.31)	5.59 (5.36)	14.79 (14.51)	66
Co(L) ₂ (H ₂ O) ₂ [5]	Orange	185 – 186	50.73 (50.54)	5.59 (5.63)	14.79 (14.63)	82

^acalculated values are in parentheses.



Scheme-1: Preparative method for (E)-1-(2,4-dinitrophenyl)-2-(1,7,7-trimethylbicyclo[2.2.1]heptan-2-ylidene)hydrazine.

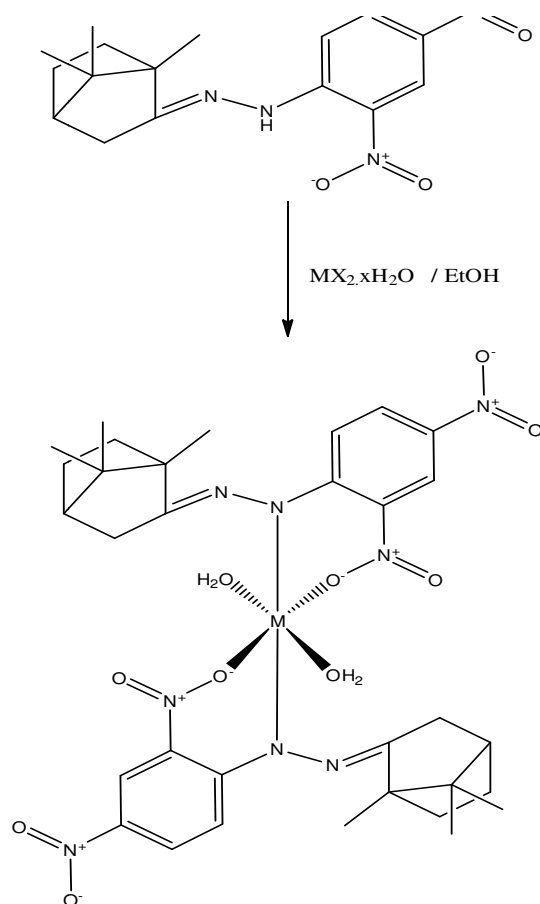


Scheme-2: General mechanism to form hydrazones compounds.

(E)- 1-(2,4-dinitrophenyl)- 2-(1,7,7-trimethylbicyclo [2. 2. 1] heptan-2-ylidene) hydrazine may be crystalline to way what's more may be dissolvable done such as way regular solvents. Its confined constantly on around described. Furthermore crystalline edifices for Copper (II), Nickel (II), Cobalt (II), Zinc (II) and iron (II) particles. The after effects of essential examination (CHN) with sub-atomic structure and the dissolving keeps tabs need aid presented to Table-1. The conclusions obtained would over incredible simultaneousness for the individuals figured for the recommended mathematical statement and the softening concentrates need aid sharp,

demonstrating the ethicalness of the orchestrated hydrazone and their edifices. Those structures of the hydrazone and their structures under investigation need aid provided for underneath (Scheme-3). Those structures about these mixes will be moreover asserted Eventually IR and ^1H NMR spectra, which will a chance to be analyzed on a nitty gritty route.

Infrared spectra: The IR spectra of ligand and their complexes are presented in Table-2. The IR spectra of the ligands and complexes synthesized are shows strong band appeared at range $(2958 - 2968) \text{ cm}^{-1}$ and $(3041-3107) \text{ cm}^{-1}$ due to stretching aliphatic (C-H) and aromatic (C-H)^{29,30}. The IR spectra of the complexes were compared with of the free ligand (L) in order to determine the coordination sites that may be involved in chelating. There was some guide peaks in the spectra of the ligands, which were helpful in achieving this goal. The position and/or the intensities of these peaks are expected to change upon chelating. New peak is also guide peak, as M-N and M-O in chelating.



Where $\text{MX}_2 \cdot x\text{H}_2\text{O} = \text{NiCl}_2 \cdot 6\text{H}_2\text{O}; \text{CoCl}_2 \cdot 6\text{H}_2\text{O}; \text{CuBr}_2; \text{ZnCl}_2$ or FeCl_2

Scheme-3: Preparative techniques for edifices (1:2) molar proportion.

Table-2 are showed this guide apex. Upon relationship, these band was moved to higher or lower wave numbers in the structures, showing the participation of the nitrogen in coordination (M-N)^{29,30}. Several medium appeared in the (464 - 482) cm⁻¹ region of the spectra are a direct result of the stretching (M—N) bond^{29,30}. New aggregation are found in the spectra of the structures in the zones (505 - 518) cm⁻¹ which are allotted to ν (M-O) amplifying vibrations for metal structures^{29,30}. The IR spectra of the ligand and buildings incorporated are shows two aggregation appeared at range (1049 - 1107) cm⁻¹ and (1610 - 1739) cm⁻¹ in light of augmenting aliphatic (C-N) and (C=N) respectively^{29,30}. Therefore; from the IR spectra it is assumed that the ligand carries on as a fair bidentate ligand encouraged to the metal molecule by method for N and O particle in nitro aggregate^{29,30}. The IR spectra for ligand and it's complexes as shown in Figure-1-6.

¹H NMR spectra: ¹H NMR spectra in deturated DMSO are given in Table-1 explain in Figure-7–13 and band data in Table-3. The ¹H NMR spectra of the hydrazone in DMSO indicates doublet signals inside the 7.48 ppm and 8.58 ppm are refers to H18 and H15 in complexes while in ligand appeared as doublet signals at 7.97 ppm and 8.67 ppm. H17 has been appeared in 7.99 ppm as doublet signals in ligand while in complexes have been showed at 8.45 as quartet signals. The spectra of the structures are differed in Comparison with those of the parent compound (hydrazone). The ¹H NMR spectra of the hydrazone united from camphor and 2,4-dinitrophenyl hydrazine revealed a banner at 9.63 ppm (singlet) in light of the proton NH and The proton NH has vanished in ¹H NMR spectra of structures hydrazone, demonstrating that the NH proton is removed by chelation with the metal ion^{29,30}.

Table-2: Data of IR Spectra for Ligand and compounds 1-5.

Ligand/ complexes IR (cm ⁻¹)	λ_{\max} in nm (ϵ in M ⁻¹ cm ⁻¹)
Ligand (L)	3086 (C-H) Ar., 2958 (C-H) aliph., 1489 (C=C) Ar., 3323 (N-H), 1739 (C=N), 1107 (C-N) aliph., 1570 (N=O), 1389 (N-O).
Cu(L) ₂ (H ₂ O) ₂ [1]	3088 (C-H) Ar., 2964 (C-H) aliph., 1419 (C=C) Ar., 3352 (O-H), 1612 (C=N), 1058 (C-N) aliph., 1535 (N=O), 1332 (N-O), 464 (M-N), 505 (M-O).
Fe(L) ₂ (H ₂ O) ₂ [2]	3088 (C-H) Ar., 2958 (C-H) aliph., 1421 (C=C) Ar., 3421 (O-H), 1612 (C=N), 1049 (C-N) aliph., 1539 (N=O), 1336 (N-O), 482 (M-N), 518 (M-O).
Zn(L) ₂ (H ₂ O) ₂ [3]	3041 (C-H) Ar., 2964 (C-H) aliph., 1419 (C=C) Ar., 3551 (O-H), 1610 (C=N), 1053 (C-N) aliph., 1541 (N=O), 1340 (N-O), 482 (M-N), 518 (M-O).
Ni(L) ₂ (H ₂ O) ₂ [4]	3107 (C-H) Ar., 2960 (C-H) aliph., 1419 (C=C) Ar., 3336 (O-H), 1614 (C=N), 1060 (C-N) aliph., 1543 (N=O), 1332 (N-O), 478 (M-N), 514 (M-O).
Co(L) ₂ (H ₂ O) ₂ [5]	3095 (C-H) Ar., 2968 (C-H) aliph., 1419 (C=C) Ar., 3336 (O-H), 1616 (C=N), 1058 (C-N) aliph., 1543 (N=O), 1332 (N-O), 478 (M-N), 514 (M-O).

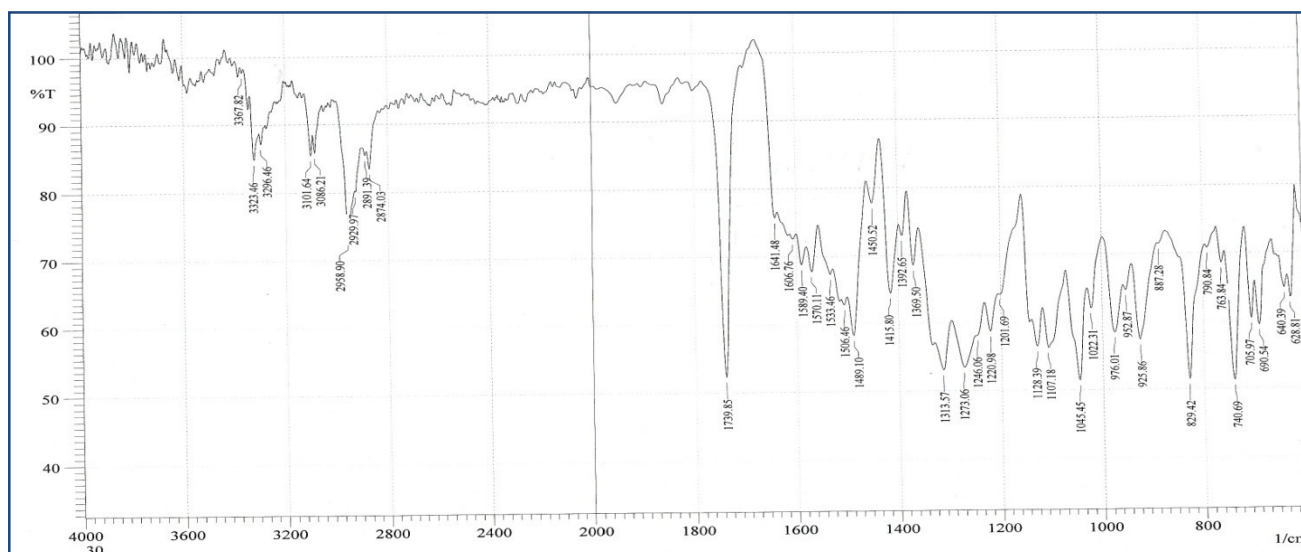


Figure-1: IR spectra for ligand.

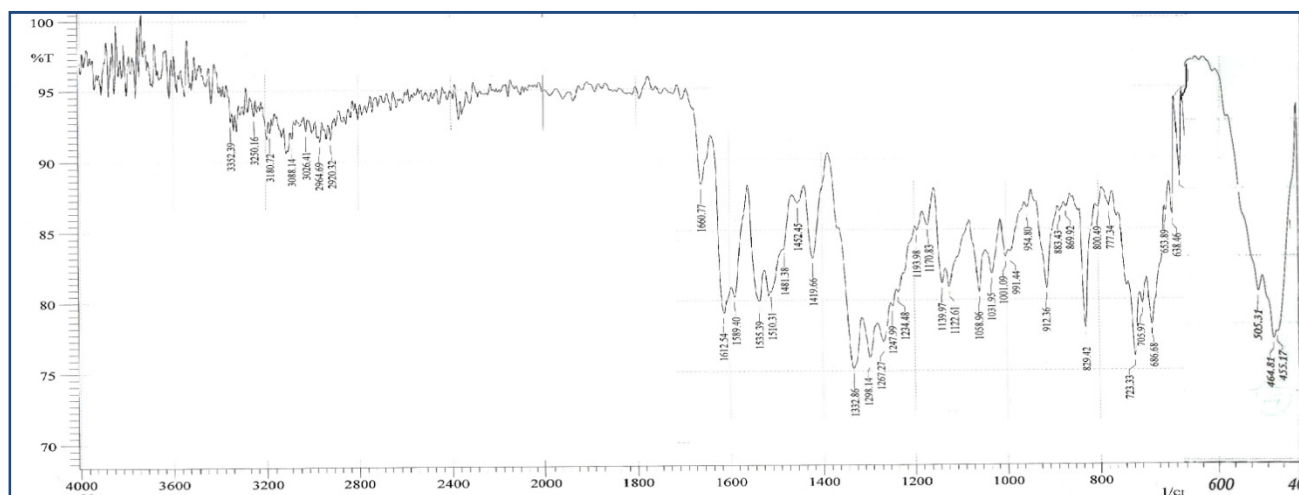


Figure-2: IR spectra for Complex 1.

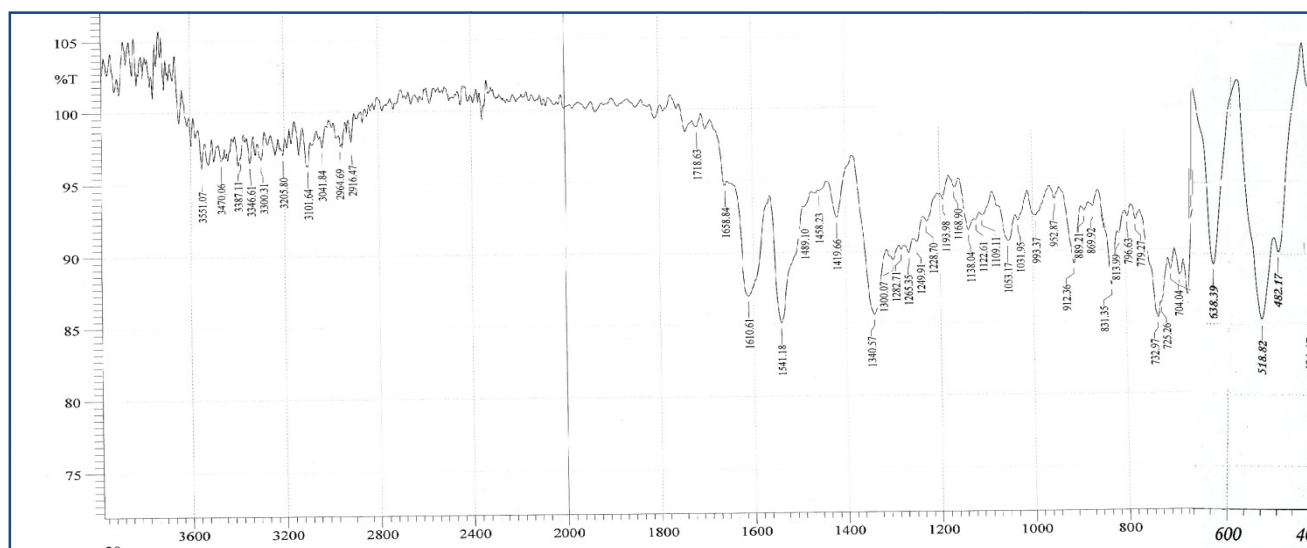


Figure-3: IR spectra for Complex 2.

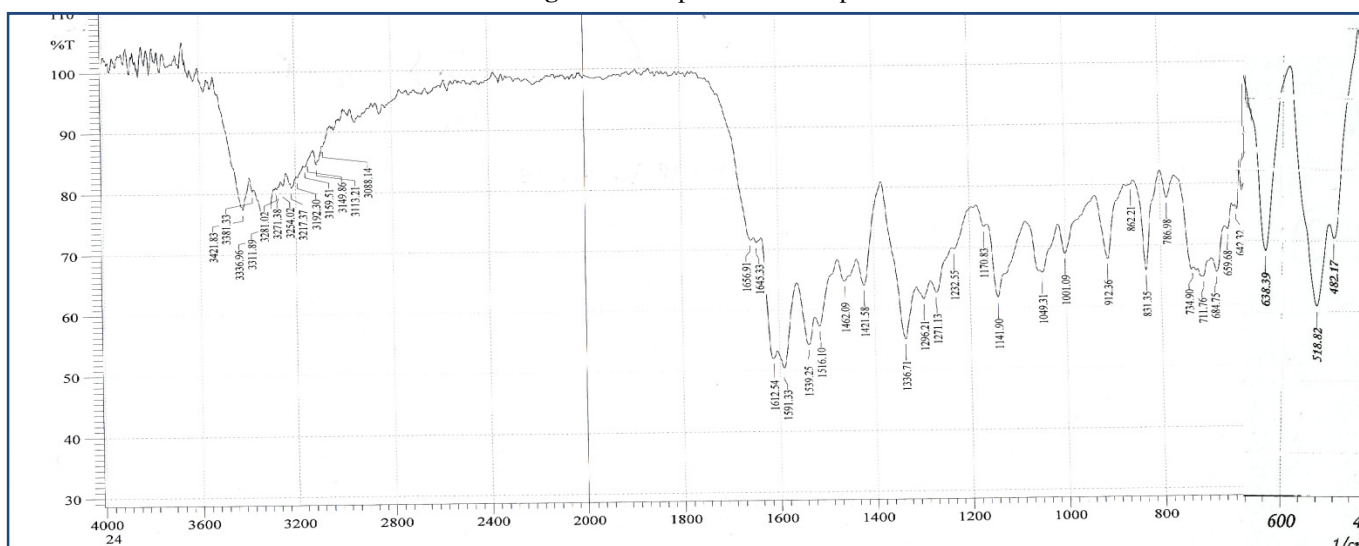


Figure-4: IR spectra for Complex 3.

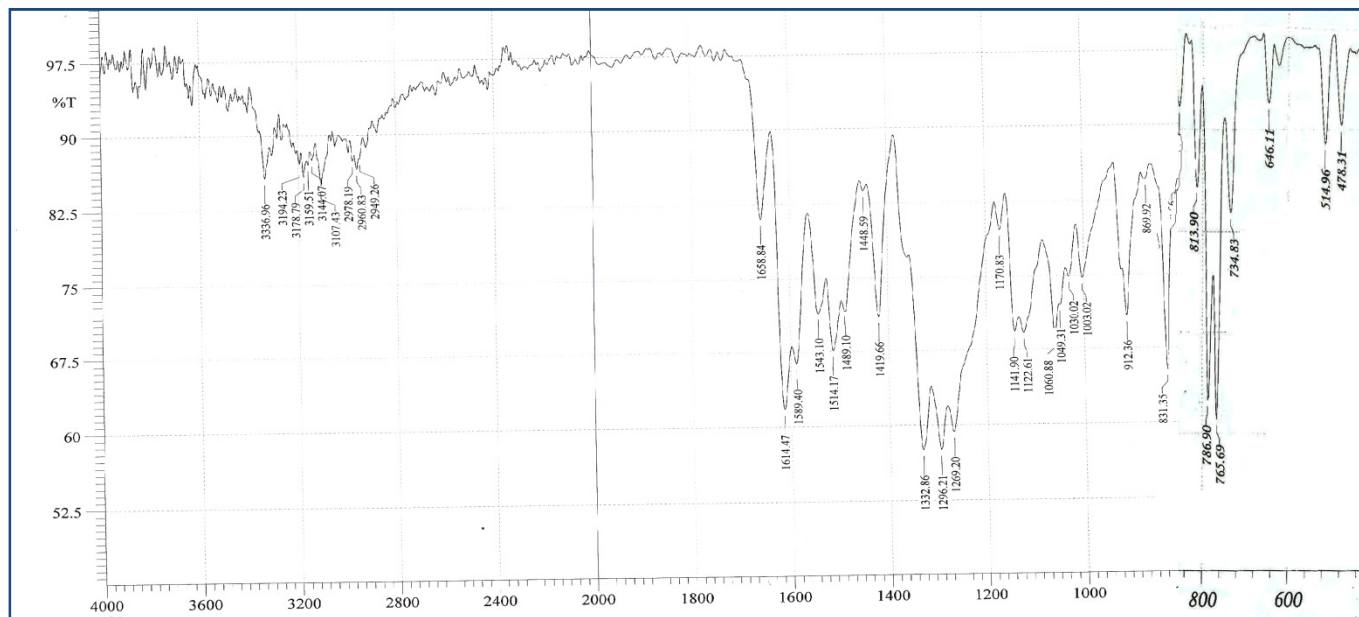


Figure-5: IR spectra for Complex 4.

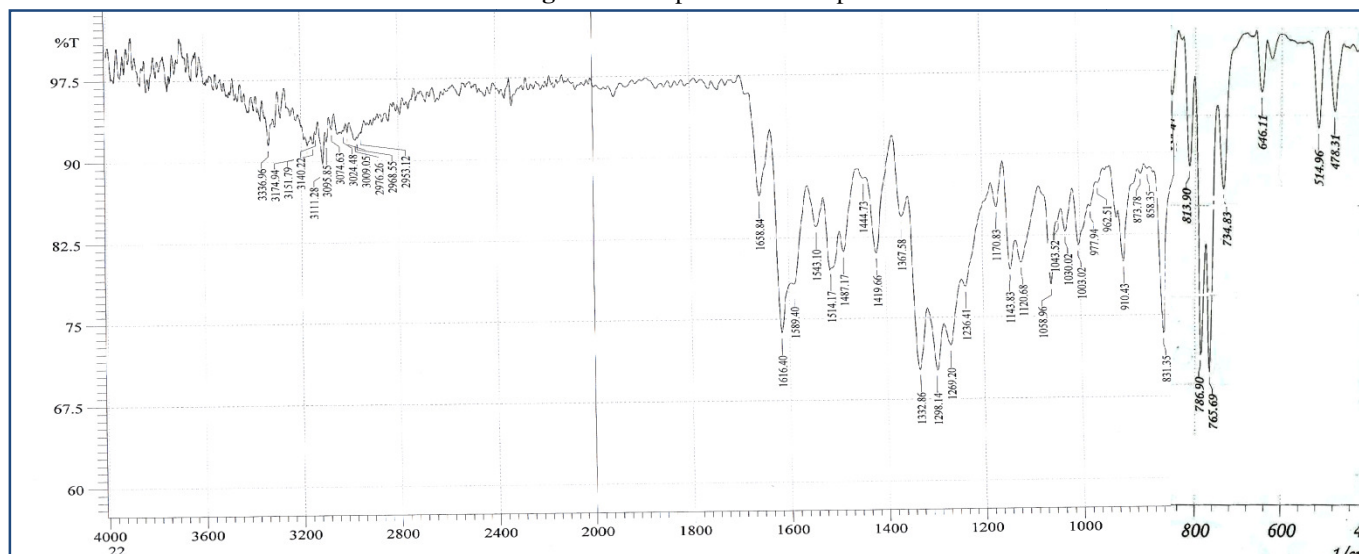


Figure-6: IR spectra for Complex 5.

Table-3: ¹H NMR Spectroscopic data for Ligand and compounds 1-5.

Ligand/ complexes	Chemical shift (ppm)
Ligand (L)	0.94 (S, 3H,1), 0.95 – 1.10 (m, 6H, 10 & 11), 1.44 – 1.55 (m, 2H, 5), 2.69 – 2.73 (m, 4H, 7 & 8), 7.97 (d, 1H, 17), 8.67 (d, 1H, 18), 8.58 (d, 1H, 15), 9.63 (s, 1H, 12)
Cu(L) ₂ (H ₂ O) ₂ [1]	0.88 (S, 6H,1), 0.93 (d, 12H, 10 & 11), 1.86 – 1.91 (m, 4H, 5), 1.95 – 2.03 (m, 4H, 7), 1.35 – 1.41 (m, 4H, 8), 7.48 (d, 2H, 17), 8.45 (q, 2H, 18), 8.58 (d, 1H, 15)
Fe(L) ₂ (H ₂ O) ₂ [2]	0.88 (S, 6H,1), 0.93 (d, 12H, 10 & 11), 1.86 – 1.91 (m, 4H, 5), 1.95 – 2.03 (m, 4H, 7), 1.35 – 1.41 (m, 4H, 8), 7.48 (d, 2H, 17), 8.45 (q, 2H, 18), 8.58 (d, 1H, 15)
Zn(L) ₂ (H ₂ O) ₂ [3]	0.88 (S, 6H,1), 0.93 (d, 12H, 10 & 11), 1.86 – 1.91 (m, 4H, 5), 1.95 – 2.03 (m, 4H, 7), 1.35 – 1.41 (m, 4H, 8), 7.48 (d, 2H, 17), 8.45 (q, 2H, 18), 8.58 (d, 1H, 15)
Ni(L) ₂ (H ₂ O) ₂ [4]	0.88 (S, 6H,1), 0.93 (d, 12H, 10 & 11), 1.86 – 1.91 (m, 4H, 5), 1.95 – 2.03 (m, 4H, 7), 1.35 – 1.41 (m, 4H, 8), 7.48 (d, 2H, 17), 8.45 (q, 2H, 18), 8.58 (d, 1H, 15)
Co(L) ₂ (H ₂ O) ₂ [5]	0.88 (S, 6H,1), 0.93 (d, 12H, 10 & 11), 1.86 – 1.91 (m, 4H, 5), 1.95 – 2.03 (m, 4H, 7), 1.35 – 1.41 (m, 4H, 8), 7.48 (d, 2H, 17), 8.45 (q, 2H, 18), 8.58 (d, 1H, 15)

The spectra of the critical number of mixes display a singlet signals at the degree 0.94 ppm and 0.88 ppm in light of the protons CH_3 (H1) of the ligand in hydrazone and it's structures respectively. The doublet signals at 0.93 ppm proposed the attribution of the proton of the CH_3 - (H10 and H11) in all new complexes were prepared while the CH_3 - (H10 and H11) in ligand has been appeared at the range (0.95 – 1.10) as multiple signals²⁹. The spectra of the number of blends exhibit a different banner at the range 1.86 – 1.91 ppm, 1.95 – 2.03 ppm and 1.35 – 1.41 ppm due to the protons CH and CH_2 - (H5, H7 and H8) of the hydrazone compound in complexes respectively but in hydrazone ligand has been showed at the range 1.44 – 1.55 ppm and 2.69 – 2.73 ppm for H5, H7 and H8 respectively²⁹. The ^1H NMR spectrum of ligand, Figure-8, showed a doublet signals at 7.97 ppm, 8.67 ppm and 8.58 ppm, corresponding to the phenyl protons (H17, H18 and H15). A doublet signal centered at 7.48 ppm and 8.58 ppm due to H17 and H15 in all complexes referring to phenyl ring while the quartet signal can be appeared at 8.45 ppm due to H18 in all complexes^{29,30}. Table-3 and Figure- (7-13). Observed through spectroscopic study that all

new complexes prepared have the same frequency of the protons due to the similarity of ligand used in the preparation of these complexes.

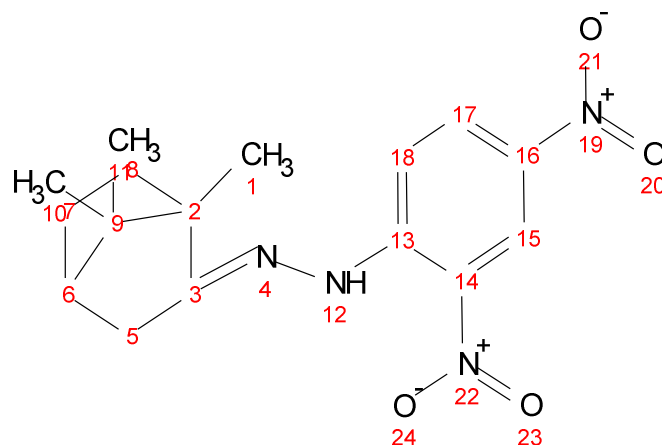


Figure-7: Ligand form with tags.

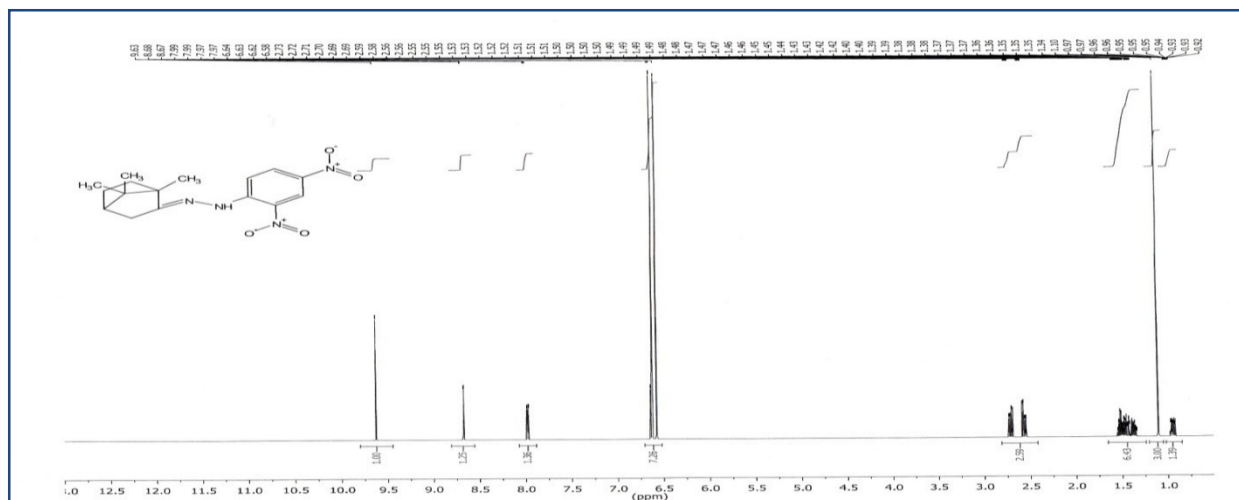


Figure-8: ^1H NMR spectra for ligand.

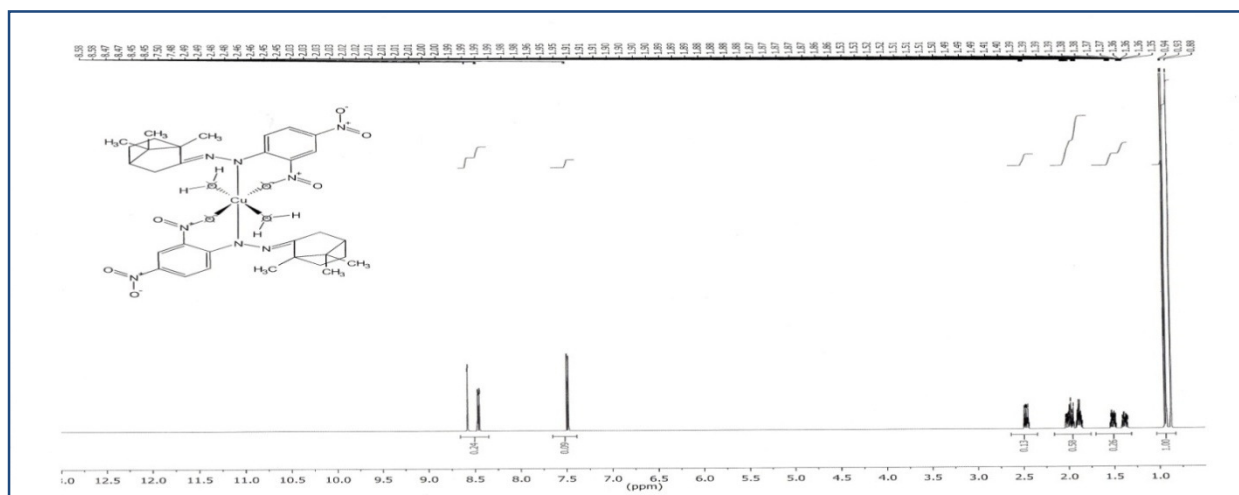


Figure-9: ^1H NMR spectra for complex 1.

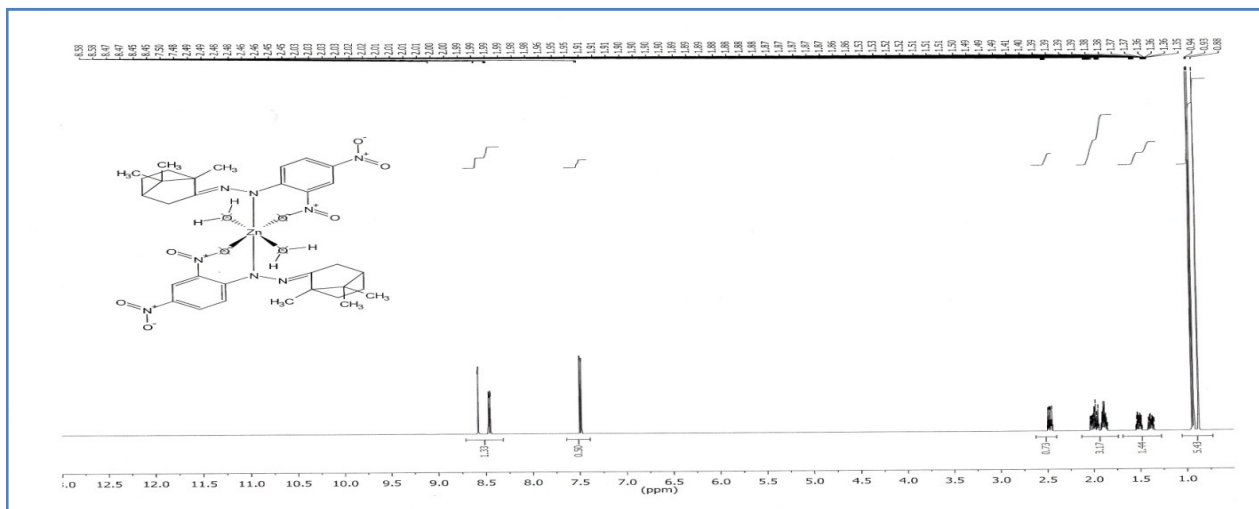


Figure-10: ^1H NMR spectra for complex 2.

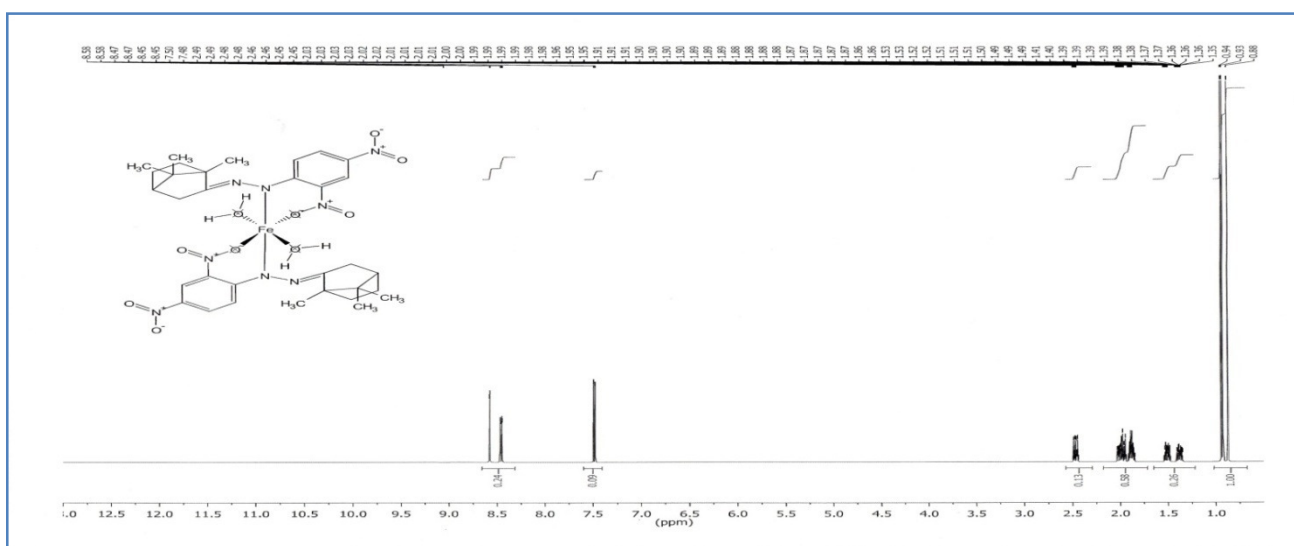


Figure-11: ^1H NMR spectra for complex 3.

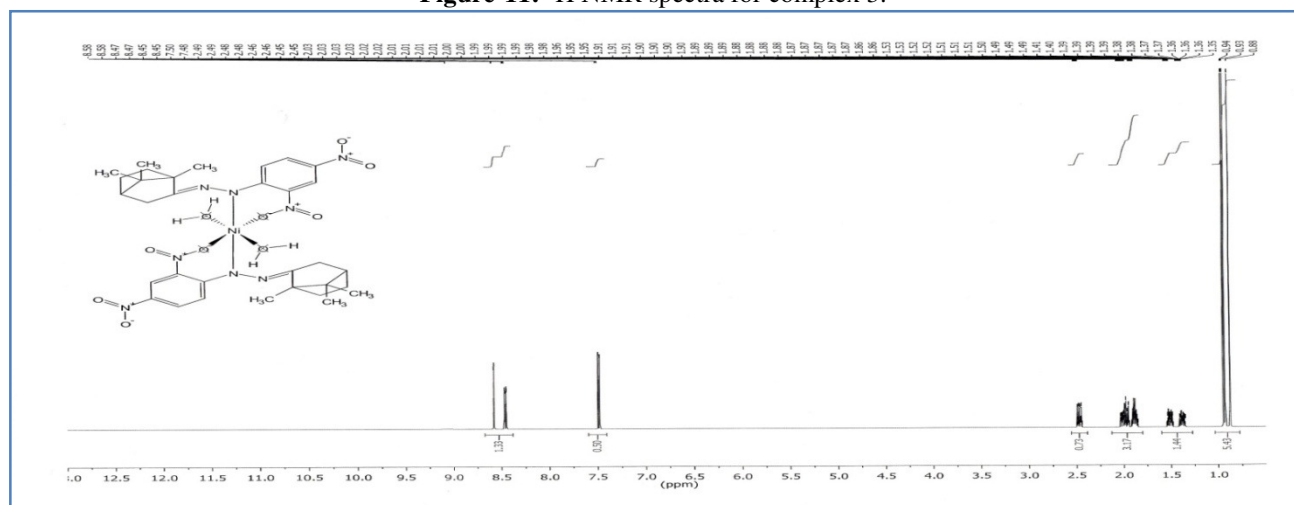


Figure-12: ^1H NMR spectra for complex 4.

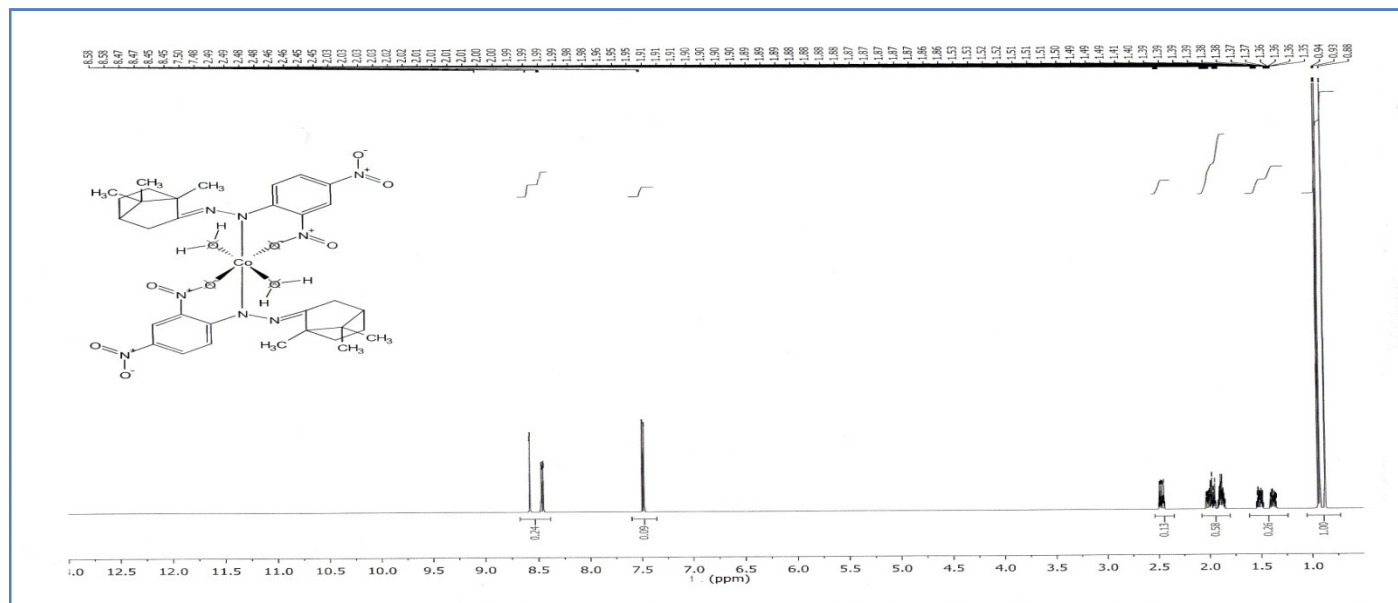


Figure-13: ^1H NMR spectra for complex 5.

Conclusion

Another hydrazone ligand has been set up by the development of camphor with 4-dinitrophenyl hydrazine. Logical IR, ^1H NMR and elemental examination (CHN) revealed a 1:2 thing. Hydrazones and their subordinators constitute an adaptable class of blends in common science. In another review that blends have interesting natural properties, for instance, quieting, torment easing, anticonvulsant, antituberculous, antitumor, against HIV and antimicrobial development. Hydrazones are crucial blends for pharmaceutical arrangement, as could be permitted ligands for metal structures, organocatalysis besides for the amalgamations of heterocyclic blends.

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