

Synthesis, Characterization and EPR Study of Some Transition Metal Complexes with N-O Donor Lewis Base of Isonozide.

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Abstract

A series of new complexes of the type $[\text{Cu}(\text{L})_2]\text{Cl}_2$ (1), $[\text{Ni}(\text{L})\text{Cl}_2]\cdot\text{H}_2\text{O}$ (2), $[\text{Co}(\text{L})_2(\text{H}_2\text{O})_2]\text{Cl}_2$ (3), $[\text{Mn}(\text{L})_2(\text{H}_2\text{O})_2]$ (4), $[\text{Zn}(\text{L})_2\text{Cl}_2]$ (5), where L is N-(phthalimidyl) isonicotinamide have been synthesized and characterized by magnetic moment, molar conductivity UV, and (FT-IR) and some of them were characterized by EPR spectroscopy. Ligand was characterized by FT-IR, ¹HNMR and ¹³CNMR spectroscopy. The spectroscopic data indicated that the isoniazide ligand act as bidentate N,O donors and the complexes (2-5) are paramagnetic and the complex(6) diamagnetic. The optimization of their structures indicated that the geometry of complex (1) is square planar and tetrahedral for complex (2) and octahedral for complexes (3-5). [DOI: [10.22401/ANJS.00.1.02](https://doi.org/10.22401/ANJS.00.1.02)]

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1- Introduction

Tuberculosis is one of the most important problems affecting health. It is classified as the second leading cause of death in the world among infectious disease [1]. In 2013, 9 million people were diagnosed with TB, 1.5 million of whom died from the disease. Isoniazid (INH) is the best choice for the treatment of TB and it plays a vital role in effective control of TB.[2].

Hydrazones belong to the azomethane class of compounds have attracted the attention of many chemists because of their broad spectrum of drug activity properties with structural flexibility and associative behavior.

Hydrazones are known as compounds containing two interrelated $\text{R}_1\text{CN-NR}_2$ nitrogen atoms, as they could act as anti-microbial, antitubercular and antitumor agents [3-6]. After the cornerstone of anti-TB therapy has been used for more than half a century, much has been learned about biochemistry and multifaceted ways to act as isoniazid front-line drugs. In fact, with the massive world TB burden and the alarming rise in the number of clinical isolates that show drug resistance or increased virulence [7-10]. Isoniazid has become the most researched anti tubercular agent, [11-13].

Isonicotinoylhydrazide (INH) is considered one of the strongest and best anti-TB drugs and works to kill *M. tuberculosis*.

Isonicotinoylhydrazone derivatives containing heterogeneous components have been found to possess the best anti-TB activity [14,15].

The clinical benefit of isoniazid (isonicotinic acid hydrazide) was discovered in the 1950's when its high anti-tuberculosis efficacy was first observed [16], higher than any other compound used at the time [17-20]. INH is indeed particularly active against *Mtb* with a minimum concentration for inhibition (MIC) of 0.05 mg/mL [18]. Imides of aromatic dicarboxylic acids are important in the construction of macromolecules 1,2 as well as supramolecular assembly [21-24]. As cancer cells are highly proliferative tissues, one of the most promising biological targets to decrease tumor cell growth is the DNA. Naphthalimide derivatives was among the few compounds that interact with DNA and it Has gained considerable interest based on the properties of the DNA- intercalating and topoisomerase-poisoning activities, [25].

Cyclic imides have great importance because their various compounds have a wide range of biological activities, [26,27].

This work aimed to synthesize a potential ligand containing both, isonicotinoylhydrazide and phthalimidyl moieties and synthesis of new transition metal complexes from this ligand. Thus, the present investigation throw light on synthesis,

characterization, EPR study of novel N-(phthalimidyl) isonicotinamide complexes.

2- Experimental

2-1 chemicals

Chemicals used in this work are supplied from BDH and Fluka companies and are used without further purification.

2-2 Physical measurements

Gallenkamp apparatus were used for determine melting points of prepared compounds and were uncorrected. FTIR spectra were recorded in Baghdad University on SHIMADZU FTIR-8400 Fourier Transform Infrared spectrophotometer using KBr discs. ^1H NMR and ^{13}C NMR spectra were recorded on Bruker 500MHz-Avance III instrument using DMSO- d_6 as a solvent and TMS as internal reference in the university of Jordan faculty of science. EPR spectra of Cu(II) and Ni(II) complexes were recorded as poly crystalline sample in the DMF solution on conventional X-band Bruker Elexsys E 500 CW-spectromwter in En-shams university laboratories.

2-3 Synthesis of ligand

In 250 mL Glacial acetic acid a mixture of (0.013 mole, 0.493g) of phthalic anhydride and (0.013 mole, 0.457g) of isoniazid was reflexed for 6 h. then cooled to room temperature and pour into ice water. The white precipitate of the ligand Fig. (1) was separated, washed with 5% sodium bicarbonate and recrystallized from ethanol. Yield: 90%, m.p.: 220-222 °C, [28,29].

2-4 Synthesis of $[\text{Cu}(\text{L})_2]\text{Cl}_2$

(0.002 mole, 0.53 g) of ligand was dissolved in 25 mL absolute ethanol. To this solution the ethanolic solution of copper salt ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$) (0.001 mole, 0.17 g) was added. The mixture was refluxed with stirring for 2h. After cooling to room temperature a green complex of cupper (II) precipitated out. It was filtered, washed with ethanol and dried over P_4O_{10} under vacuum. Yield : 83% , m. p.: 276-278 °C, [30].

2-5 Synthesis of $[\text{Ni}(\text{L})\text{Cl}_2] \cdot \text{H}_2\text{O}$

(0.001 mole, 0.27 g) of ligand was dissolved in 25 mL absolute ethanol. To this solution the ethanolic solution of corresponding salts (0.001 mole) was added. The pH of solution was adjustment to 7 with sodium carbonate then the mixture was refluxed with stirring for 2h. After cooling to room temperature a colored complex precipitated out. It was filtered, washed with ethanol and dried over P_4O_{10} under vacuum. Yield: 80%, m. p.: 263-265 °C.

2-6 Synthesis of $[\text{Co}(\text{L})_2(\text{H}_2\text{O})_2]\text{Cl}_2$

The complex of Co(II) was synthesized following the same procedure in (2-5), but by using the ratio of 2:1 from ligand to salt. Yield: 78%, m. p.:322-324 °C.

2-7 Synthesis of $[\text{Mn}(\text{L})_2(\text{H}_2\text{O})_2]$

The complex of Mn(II) was synthesized following the same procedure in (2-5), but by using the ratio of 2:1 from ligand to salt. Yield: 75% , m. p.: 257-259 °C.

2-8 Synthesis of $[\text{Zn}(\text{L})_2\text{Cl}_2]$

The complex of Zn(II) was synthesized following the same procedure in (2-5), but by using the ratio of 2:1 from ligand to salt. Yield: 76%, m.p.:347-349 °C. Physical properties of prepared compound are listed in Table (2).

3- Result and discussion

3-1 FT-IR, ^1H NMR and ^{13}C NMR spectra

FT-IR spectrum of the ligand Fig.(2) showed strong absorption bands at 1724 cm^{-1} and 1687 cm^{-1} assigning to $\nu(\text{C}=\text{O})$ of phthalimide and $\nu(\text{C}=\text{O})$ of amide respectively. The vibration of (N-H) group was showed at 3271 cm^{-1} . [31].

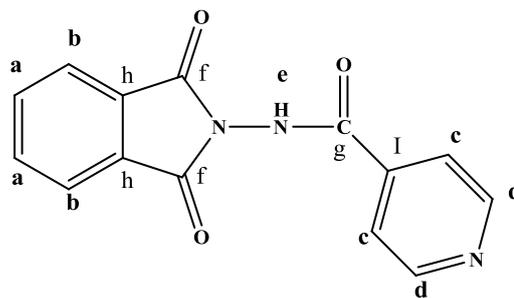


Fig.(1) Structure of ligand.

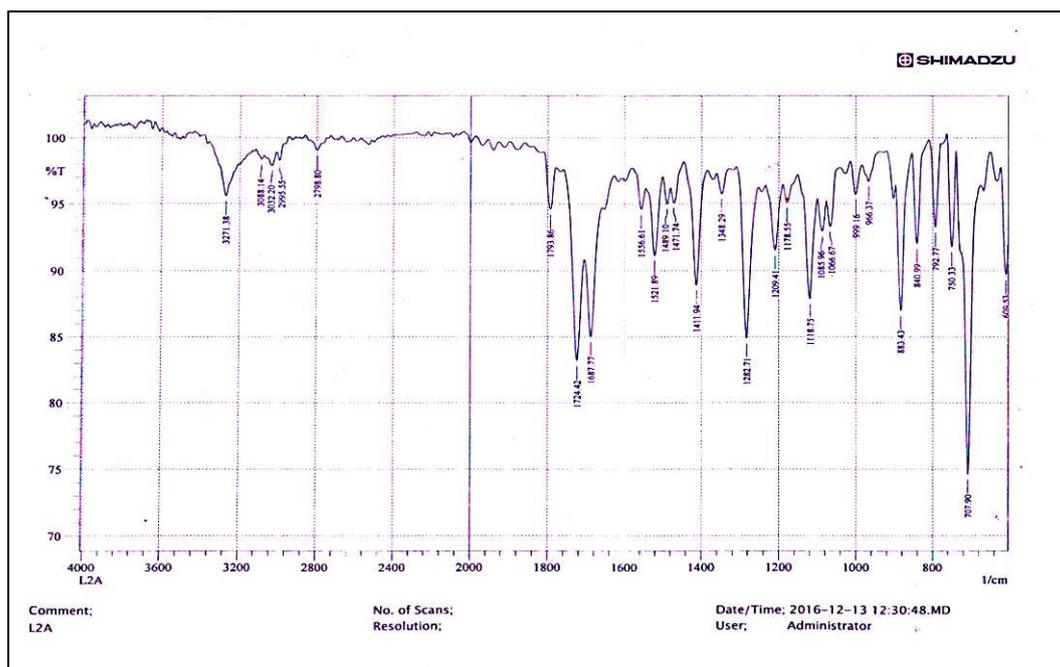


Fig.(2) FT-IR for ligand.

¹HNMR spectrum for ligand Fig.(3) showed characteristic signals at $\delta = (7.87-8.02)$ ppm due to aromatic protons (a, b, c), at $\delta = (8.85)$ ppm belong to aromatic protons (d) of pyridine ring, at $\delta = (11.7)$ ppm belong to (NH) proton. ¹³CNMR spectrum for ligand

Fig.(4) showed characteristic signals at $\delta = (121.9, 124.45, 129.89, 135.97, 138.18, 151.23)$ ppm due to aromatic carbons (c, b, a, h, I, d) respectively, at $\delta = (164.66, 165.51)$ ppm belong to amide carbonyl (g) and imide carbonyl (f), respectively.

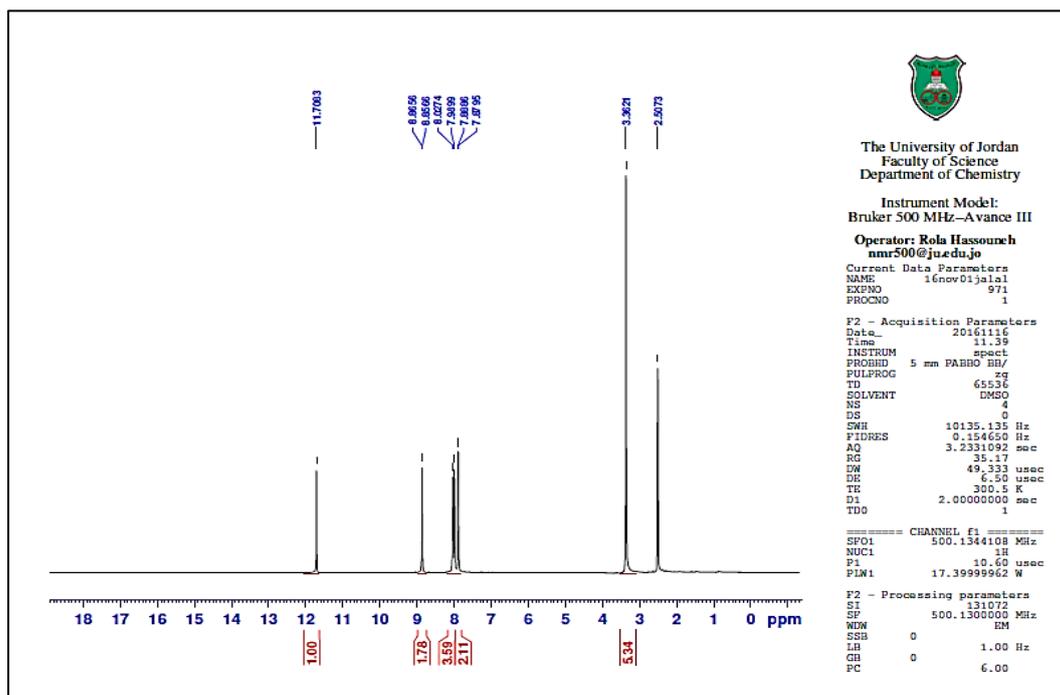


Fig.(3) ¹HNMR of Ligand.

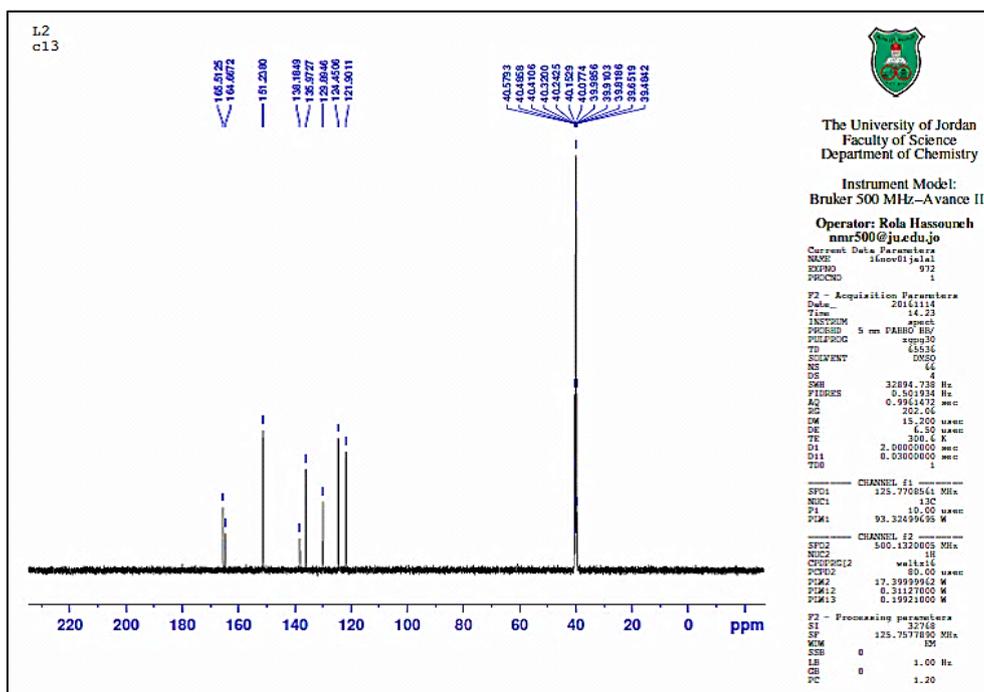


Fig.(4) ^{13}C NMR for ligand.

The FT-IR spectra of all metal complexes exhibited remarkable changes in the positions and intensities of carbonyl and imine moieties.

The manganese (II) complex $[\text{Mn}(\text{L})_2(\text{H}_2\text{O})_2]\text{Cl}_2$ showed a broad band around 3564 cm^{-1} assigning the ν (OH) group of coordinated water [32].

As well as, the lowering in the stretching frequency of (C=O) to $(1647\text{-}1627)\text{ cm}^{-1}$ assigning the bonding of oxygen atom of carbonyl with Mn (II) ion.

The solid complex of copper (II) exhibited strong absorption bands $(1745\text{-}1706)\text{ cm}^{-1}$ and $(1616\text{-}1556)\text{ cm}^{-1}$ confirmed the depression of ν (C=O) upon coordination with copper (II) complex which is square-planer symmetry [33-35].

The nickel (II) and zinc (II) complexes showed strong absorptions around $(1652\text{-}1631)\text{ cm}^{-1}$, $(1734\text{-}1685)\text{ cm}^{-1}$, $(1595\text{-}1515)\text{ cm}^{-1}$, due to ν (C=O). However, The weak absorption at $(325\text{-}286)\text{ cm}^{-1}$ and $(273\text{-}300)\text{ cm}^{-1}$ which are assigned to ν (Ni-Cl) and ν (Zn-Cl), respectively. These data confirmed the presence of chloro ligands in the constructions of these complexes. All the metal complexes, Table (1) showed medium to weak bands in the region of $(401\text{-}586)\text{ cm}^{-1}$, and $(379\text{-}497)\text{ cm}^{-1}$, which are belong to the coordination bonds of (M-N) and (M-O) respectively, [32]. However, the bending of δ (OH) for coordination water in manganese (II) and cobalt (II) complexes were appeared at $(833\text{-}1095)\text{ cm}^{-1}$. FT-IR spectral data for ligand and complexes are listed in Table (1).

Table (1)

Most characteristic observed vibrational frequencies (cm^{-1}) for ligand and prepared complexes.

No.	Compound	ν (C=O)	ν (NH)	M-O	M-N	M-Cl
1	L	1724(imide) 1687(amide)	3180-3338	–	–	–
2	$[\text{Cu}(\text{L})_2]\text{Cl}_2$	1706-1745	3166-3226	422-497(w)	524	–
3	$[\text{Ni}(\text{L})\text{Cl}_2]\cdot\text{H}_2\text{O}$	1631-1652	3305-3205	447	501	325-268(m)
4	$[\text{Co}(\text{L})_2(\text{H}_2\text{O})_2]\text{Cl}_2$	1631-1649	3413-3415	366(m)	401-4018	–
5	$[\text{Mn}(\text{L})_2(\text{H}_2\text{O})_2]$	1627-1647(sh)	1596(s)	424-442	586	–
6	$[\text{Zn}(\text{L})_2\text{Cl}_2]$	1734-1685(s) 1793(w)	3564(s)	379-404	528-561	273-300(w)

2- Magnetic moment and Electronic spectra

The free ligand (L) spectrum was estimated the it's UV-visible in (0.001M ethanol), displayed two transitions at 235 nm and 260 nm assigning to chromophore transitions $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ respectively. The solution of metal complexes in (DMSO 10^{-4} M) showed remarkable changes in the uv- visible spectra compared with the spectrum of ligand. The yellow solution of Mn(II) complex displayed two absorption at 253 nm and 353nm which are assigned to MLCT and $\pi \rightarrow \pi^*$ transition respectively; thereby supports the octahedral structure around manganese (II) ion, [36].

The pal brown solution of Co (II) in DMSO showed high intestine bands at 258nm and 360nm and no $d \rightarrow d$ transitions that should be expected around 600-800nm due to masking them by fully conjugation or resonance for ($-C=N-$), ($C=C$), and ($C=O$) involving in the structure of ligand (isonozide) Lewis base. By the same way no $d \rightarrow d$ transitions band for Ni(II) complex, which it's green solution showed three absorption bands around 245nm, 259nm, and 360nm assigned to $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$ and MLCT respectively. The solid complex of Co (II) exhibited increasing in the magnetic moment around 4.2 BM due to orbital contribution in the $(t_{2g})^5(eg)^2$ configuration, ascribed the octahedral geometry.

Furthermore, the increasing in μ_{eff} for copper (II) complex to 2.7 BM due to high spin of dx^2-y^2 in the structure of square- planer

complexes of Cu(II) ion. The high spin character present in Mn (II) complex due to magnetic moment of 5.3BM supposed the octahedral geometry of sp^3d^2 hybridization. The normal value of Ni (II) complex in the region of 2.5 BM support the regular tetrahedral structure around Ni(II) ion, since the presence of two odd electrons in the $(eg)^4(t_{2g})^4$ configuration, Table (2).

EPR- Discussion

EPR spectra of Ni(II) and Cu(II) complexes were recorded as poly crystalline sample and for DMF solution .The g_1 , g_2 , g_3 , g_4 factors observed from Fig.(5) for nickel (II) and from Fig.(6) for copper (II) complexes have increased as the magnetic field (H) increased. The presence of two odd electrons in Ni(II) ($3d^8$) [sp^3 tetrahedral] configuration led to $m_l = 3/2, 1/2, -1/2$ and $-3/2$ respectively; with length hedral $0^\circ, 45^\circ$ and 90° , respectively in the first and second derivatives of EPR for high spin complexes of nickel (II).

The EPR spectrum of copper (II) showed one derivative at $g = 2.0037$ with increasing of magnetic field, from ($H = 3612$ to 3619 G), investigating the presence of B_{1g}^2 term of square planer symmetry since the $3d^9$ in higher energy of dx^2-y^2 orbital. The B_{1g}^2 were estimated by calculation of g_I and g_{II} ; $g_I = 2[1 - (\lambda/\Delta L)]$, $g_{II} = 2[1 - (4\lambda/\Delta L)]$. Where ΔL represent the energy observed from digital of device, [30], [38-40].

Table (2)
physical properties, spectroscopic data, and magnetic moment (BM) of the synthesized ligand and complexes.

No.	compound	color	Yield %	m.p.	λ_{max}	$\Delta m \text{ Ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$	μ_{eff} (BM)
1	L	white	90	220-222	235,260	5	---
2	[Cu(L) ₂]Cl ₂	Light blue	83	276-278	896,293	85	2.2
3	[Ni(L)Cl ₂].H ₂ O	Light green	80	263-265	245, 259, 360	12	2.8
4	[Co(L) ₂ (H ₂ O) ₂]Cl ₂	Light brown	78	322-324	258, 360	78	4.2
5	[Mn(L) ₂ (H ₂ O) ₂]	Faint yellow	75	257-259	258, 353	73	5.5
6	[Zn(L) ₂]Cl ₂	white	76	347-349	239, 264	10	Diamagnetic

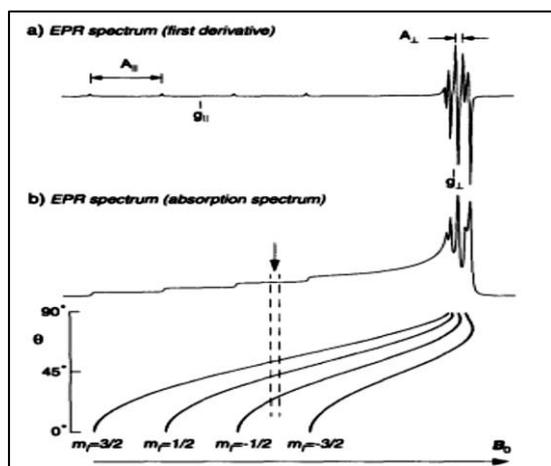


Fig. (5) Nickel(II)-g1-g4.

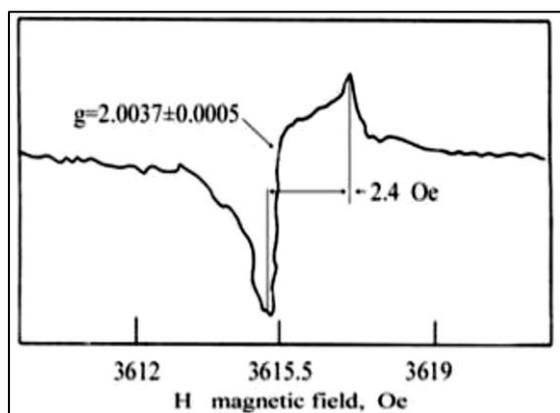


Fig.(6) Copper(II)-Sky ppt-g1-g2.

Conclusion

The infrared spectra and the resonance spectra of the proton and carbon demonstrated the agreement of prepared ligand with the proposed structure. Molecular conductivity measurements, magnetic resonance, FT-IR, ^1H NMR, ^{13}C NMR, EPR spectra, showed that the shapes of the prepared complexes was square planer with copper (II) ion and the tetrahedral with nickel (II) and octahedral with both, cobalt (II), manganese (II) and zinc (II). Fig.(7) shows the proposed shapes of prepared complexes.

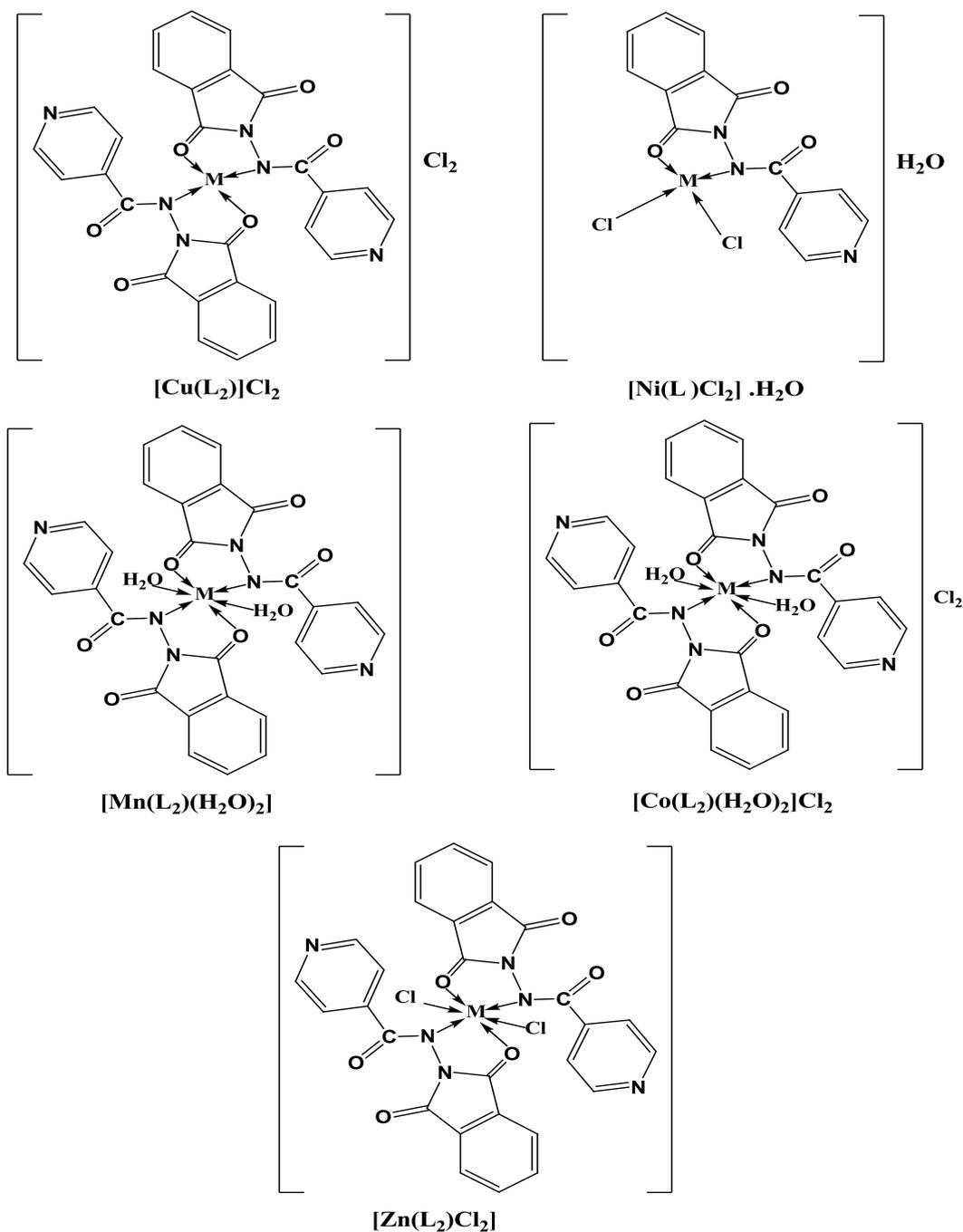


Fig.(7) Expected structures of prepared complexes.

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