

TO STUDY THE CHARACTERIZATION OF DIFFERENT METAL COMPLEXES

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ABSTRACT

Since a few years ago, metal-based medications have been utilized to treat diseases, but the main obstacle was the lack of a differentiation between therapeutic and hazardous levels. Undoubtedly, one of our society's top health issues has been cancer, which is currently the main focus of medicinal chemistry. The complexes were stated to contain histidine coordinated by two negatively charged N donor atoms out of four N donor atoms. Tetrahedral shape was preferred in the complex over octahedral geometry, which was explained based on a reduction in charge repulsion and minimization of steric crowding. Sigel H and McCormick DB used NMR spectroscopy to investigate the Cu(II)-His (1:2) combination. Comparing the complex's structure to those of other partially blocked histidine systems revealed that the tridentate histidine had coordinated to Cu(II) in a mixed manner, with one histidine molecule acting as a glycine-like and the other as a histamine-like ligand. Mn(II), Co(II), and Ni(II) complexes of L-histidine were synthesized and characterized via thermal decomposition. By transforming toxic metals like mercury, arsenic, and lead into a soluble, chemically inert form—typically a chelate—that can be expelled without further contact with the body, chelation treatment has proved effective in helping to detoxify these harmful metals. Long-term blood transfusion therapy will result in iron overload in patients with thalassemia, which has been treated with iron chelating drugs. excellent iron chelation ability in vitro and in vivo with excellent selectivity is exhibited by the tridentate chelator pyridoxal isonicotinoyl hydrazone (PIH). Numerous new iron chelating compounds of the pyridoxal isonicotinoyl hydrazone class have biological effects such antitumor, anticancer, and antimalarial action, as well as cytotoxicity, cell proliferation differentiation, and immunology.

KEY WORDS: *Metal Complexes, Pyridoxal Isonicotinoyl Hydrazone, iron chelating drugs.*

1. INTRODUCTION

One of the three naturally occurring forms of vitamin B6 is pyridoxal. From its derivatives, transition metal complexes might be produced that had desirable chemical and biological characteristics. Many scientists have

focused a lot of their attention on the complexes of Schiff bases formed from pyridoxal and amines because they can be used as models for comprehending a variety of biological events that are mediated by enzymes. The physiologically active form of pyridoxal is pyridoxal phosphate (PLP), which, in the presence of specific metal ions, functions as a co-enzyme and catalyzes numerous metabolic processes. It has been discovered that Schiff bases generated from pyridoxal and aminoguanidine show promise in the treatment of diabetic problems. Similar results were seen with the Co(II) combination of pyridoxal S-methyl thiosemicarbazone against pathogenic microorganisms. Additionally, the U937 human cell lines' ability to proliferate was hindered by the Cu(II) complexes of PLTSC and its ethyl and dimethyl variants.

Pyridoxal semicarbazone (PLSC), Pyridoxal thiosemicarbazone (PLTSC), and their binary complexes with a number of transition metals have all been studied as pyridoxal Schiff base compounds. These ligands' capacity to form stable complexes with a variety of metals, set of donor atoms, and coordinated ligand reactions make their coordination chemistry appear to be highly intriguing.

With two identical ligands, phenolic oxygen and azomethine nitrogen, and a third donor atom that is either the oxygen or sulfur atom of the amide or thioamide group, respectively, PLSC and PLTSC function as tridentate ligands. Two metallocycles are created when these compounds are coordinated through the three potential binding sites: a five-membered (semicarbazide derivative) and a six-membered (pyridoxilydine) metallocycle. Three different types of these ligands—neutral (H₂L), monoanionic (HL⁻), and dianionic (L₂⁻)—can be coordinated to the metal ions. Deprotonation of enol or thiol compounds produces the monoanionic form. The pyridine nitrogen is further deprotonated to produce the dianionic form, which results from the hydrogen atom moving from the phenolic OH group to the pyridine nitrogen atom. The reaction's pH and the metal ion's make-up determine the deprotonation sequence.

There have been numerous reports of complexes using PLTSC rather than PLSC. Other than the ONS/ONO ligand atoms, there have been reports of exceptions to the peculiar coordination modes of these ligands, but the coordination of the pyridine nitrogen atom has not been mentioned.

With the metal ions of copper, iron, nickel, cobalt, manganese, zinc, dioxo-vanadium, dialkyl tin, molybdenum, gold, platinum, thallium, chromium, palladium, and ruthenium, binary complexes of pyridoxal-based Schiff base ligands have been reported. The copper and iron complexes were the most prevalent of these.

In order to investigate the mixed ligand complexes involving these derivatives as primary ligands, to investigate their coordination modes, to analyze their structures, and to evaluate their biological activities, structural

characteristics, various biological, and catalytic properties of metal complexes of PLSC and PLTSC have sparked interest. L-Histidine and dipeptides were chosen as the secondary ligands because of their biological importance and complex coordination chemistry. They create stable metal complexes and function as tridentate ligands. Their transition metal compounds were said to have antioxidant, antibacterial, antifungal, and antitumor properties.

2. RESEARCH METHODOLOGY

2.1 Physical properties and elemental analysis

In given table-1, the physical properties and elemental analysis are displayed. The elemental analysis revealed that the composition of the Co(II)-PLTMBH complex is 1:1 (ML), whereas the composition of the Fe(III), Co(II), Ni(II), Cu(II), and Cd(II)-PLTMBH complexes is 1:2 (ML₂).

Table 1. Analytical data of metal complexes of PLTMBH.

Ligand/Complex	Colour	M. Pt. °C	%C- found(Cal)	%H- found(Cal)	%N- found(Cal)
PLTMBH (L)	Pale yellow	203-205	57.38 (57.60)	5.47 (5.61)	11.07 (11.26)
[Fe(L) ₂]H ₂ O	Dark brown	Dp>300	53.57 (53.79)	4.74 (4.98)	10.35 (10.46)
[Co(L)(H ₂ O) ₂ Cl]	Brown	Dp>300	42.59 (42.85)	3.68 (3.97)	8.19 (8.33)
[Ni(L) ₂]H ₂ O	Brick red	Dp>300	53.42 (53.55)	4.84 (4.95)	10.27 (10.41)
[Cu(L) ₂]	Dark green	Dp>300	53.06 (53.23)	4.61 (4.92)	10.15 (10.35)
[Zn(L) ₂]	Yellow	Dp>300	53.02 (53.11)	4.58 (4.92)	10.17 (10.32)
[Cd(L) ₂]	Yellow	Dp>300	50.12 (50.23)	4.48 (4.65)	9.52 (9.76)

3. RESULTS AND DISCUSSION

3.1 LC-MS:

The chromatogram of PLTMBH complexes revealed a single peak, indicating the compounds' purity.

The ESI(-) mass spectrum of the Fe(III)-PLTMBH complex displayed a peak at m/z 802 corresponding to $[\text{FeL}_2]^+$, a peak at m/z 431 attributed to $[\text{FeL}]^+$, and a peak at m/z 375 attributed to $[\text{C}_{18}\text{H}_{20}\text{N}_6\text{O}_6]^+$.

The ESI(+) mass spectrum of the Co(II)-PLTMBH complex revealed a peak at m/z 504 and $[\text{M}+2]^+$ at m/z 506 in a 1:3 ratio, which was ascribed to $[\text{CoL}(\text{H}_2\text{O})_2\text{Cl}]^+$. The m/z 469 peak resulted from the elimination of water molecules, m/z 434 from $[\text{CoL}]^+$, m/z 211 from $[\text{C}_{10}\text{H}_{12}\text{NO}_4]^+$, and m/z 167 from $[\text{C}_6\text{H}_2(\text{OCH}_3)_3]^+$.

The APCI(+) mass spectrum of Ni(II)-PLTMBH complex revealed a peak at m/z 825 due to $[\text{NiL}_2\text{H}_2\text{O}]^+$, a peak at m/z 807 due to $[\text{NiL}_2]^+$, and a peak at m/z 375 due to $[\text{C}_{18}\text{H}_{20}\text{N}_3\text{O}_6]^+$ ligand.

The ESI(+) mass spectrum of Cu(II) complex displayed peaks at m/z 829 owing to $[\text{CuL}_2\text{H}_2\text{O}]^+$, m/z 812 because of $[\text{CuL}_2]^+$, and m/z 438 because of $[\text{CuL}]^+$.

The APCI(+) mass spectrum of Zn(II) complex displayed peaks at m/z 813 corresponding to $[\text{ZnL}_2]^+$, m/z 439 attributable to $[\text{ZnL}]^+$, m/z 407 attributable to $[\text{ZnC}_{17}\text{H}_{17}\text{N}_3\text{O}_5]^+$, and m/z 375 attributable to $[\text{C}_{18}\text{H}_{20}\text{N}_3\text{O}_6]^+$.

The ESI(+) mass spectrum of the Cd(II) complex revealed peaks at m/z 860 due to $[\text{CdL}_2]^+$, m/z 487 due to $[\text{CdL}]^+$, and m/z 375 due to $[\text{C}_{18}\text{H}_{20}\text{N}_6\text{O}_6]$.

3.3 THERMOGRAVIMETRIC ANALYSIS:

The thermogram of the Fe(III)-PLTMBH complex revealed a weight loss of 2.34 percent up to 120 degrees Celsius, indicating the presence of one water lattice molecule. A abrupt 66.7% weight loss was observed between 300 and 480°C, followed by a gradual decomposition of the complex moiety between 480 and 1000°C. The residue remaining at 1000°C above 9.5% corresponds to metal oxide (FeO).

The thermogram of the Co(II)-PLTMBH complex reveals four stages of decomposition. The first step revealed a 7.68% weight loss between 150 and 250 degrees Celsius, indicating the presence of two coordinated water molecules. From 250 to 800 degrees Celsius, the complex moiety decomposed gradually in two stages, leaving a residue of over 14.8% cobalt oxide.

Due to one water lattice molecule, the Ni(II)-PLTMBH complex thermogram revealed a weight loss of 2.58 percent between 100 and 130 degrees Celsius. Complex decomposition can be attributed to an abrupt, drastic weight loss observed between 350 and 400 °C. The remaining residue, which corresponds to metal(Ni) ion (7.1%).

The Cu(II)-PLTMBH complex thermogram reveals a weight loss of 2.51% up to 120°C, indicating the presence of lattice water. From 280 to 700 degrees Celsius, the complex decomposes slowly in two stages, with copper oxide accounting for approximately 10.2% of the residue.

Up to 150°C, the thermogram of the Zn(II)-PLTMBH complex revealed a weight loss of 2.83 percent, indicating the loss of one mole of water. The complex underwent a rapid 74.2% decomposition between 300-400°C, followed by a gradual decomposition up to 1000°C. About 10.8% of the remaining residue corresponds to zinc oxide.

The Cd(II)-PLTMBH complex thermogram exhibited stability up to 300°C, followed by a two-step decomposition pattern. Complex moiety undergoes a precipitous weight loss between 300 and 450 degrees Celsius, and the resulting residue is 14.7% metal oxide (CdO).

3.4 IR SPECTRA:

The disappearance of a medium band corresponding to the phenolic group $\nu(\text{O-H})$ in the ligand at 3396cm^{-1} in all complexes suggests deprotonation and coordination via phenolic oxygen. This was corroborated by a $10\text{-}40\text{cm}^{-1}$ shift in the band at 1228cm^{-1} assigned to $(\text{C-O})_{\text{phenolic}}$ in the IR spectrum of all the complexes. The bands in the $3000\text{-}3500\text{cm}^{-1}$ region may be caused by (O-H) vibrations of the CH_2OH group and (N-H) vibrations of the amide group. In all the complexes, the peak corresponding to the azomethine group (C=N) at 1653cm^{-1} in the ligand spectrum has been altered to a lower frequency, indicating coordination via azomethine nitrogen. In the Co(II), Ni(II), Cu(II), Zn(II), and Cd(II) complexes of PLTMBH, the band at 1674cm^{-1} characteristic of the carbonyl group (C=O) has been shifted to a lower frequency, indicating coordination through carbonyl oxygen in the ketoform. The band corresponding to (N-H) at 3170cm^{-1} in the IR spectrum of the carbon monoxide molecule. PLTMBH appeared in the same range in all complexes, indicating that it did not participate in coordination.

Enolization of the carbonyl group has been postulated based on the disappearance of bands corresponding to (C=O) at 1674cm^{-1} and (N-H) at 3170cm^{-1} in the IR spectrum of the Fe(III)-PLTMBH complex. In addition, the formation of new bands corresponding to $(\text{C-O})_{\text{enolic}}$ at 1180cm^{-1} and (C=N) peak at 1577cm^{-1} in the Fe(III)

complex supports the coordination via enolic oxygen. In the formation of complexes, one of the ligands was monoanionic and the other was dianionic. In the dianionic form, hydrogen was deprotonated from the pyridine nitrogen (NH^+), whereas in the monoanionic form, the proton was retained. The presence of a band at 2835cm^{-1} owing to (NH^+) was observed in the Fe(III) complex. In all complex IR spectra, the far region displayed new bands owing to (M-O)phenolic, (M-N), and (M-O)enolic vibrations. The Co(II) complex exhibited vibrations of $380\text{-}350\text{cm}^{-1}$ (M- H_2O) and $320\text{-}280\text{cm}^{-1}$ (M-Cl), indicating their coordination. Thus, PLTMBH coordinates to metal ions via phenolic-O, azomethine-N, and carbonyl-O atoms, and functions as a tridentate O,N,O donor.

3.5 ^1H -NMR SPECTRUM:

Comparing the ^1H -NMR spectra of the Zn(II)-PLTMBH complex (fig.1) and the ligand revealed a shift in values indicating complex formation. The absence of the peak at 12.45ppm , which corresponds to the phenolic proton (-OH) attached to the pyridine ring, indicates deprotonation of phenolic hydrogen. The signal at 12.28ppm corresponds to the amide proton (-NH), which has appeared at 12.27ppm in the Zn(II) complex, indicating coordination via keto form. The transition of the azomethine proton ($\text{HC}=\text{N}$) from 8.94ppm to 8.91ppm in the complex indicates the coordination of azomethine nitrogen.

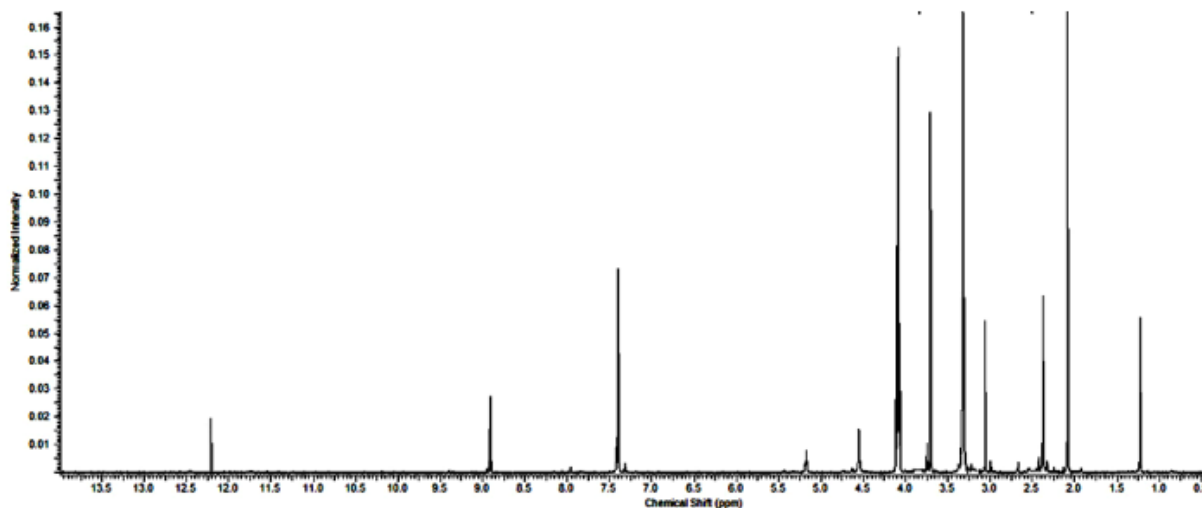


Fig.1: ^1H -NMR spectrum of Zn(II)-PLTMBH

3.6 MAGNETIC SUSCEPTIBILITY:

The magnetic moment values of Fe(III)-PLTMBH, Co(II)-PLTMBH, Ni(II)-PLTMBH, and Cu(II)-PLTMBH were determined to be 5.85BM, 3.73BM, 2.81BM, and 1.85BM, respectively, indicating their high spin nature and outer orbital complexes with five, three, two, and one unpaired electrons surrounding the metal ions, respectively.

3.6 UV-visible spectra:

The UV-visible spectrum of the Fe(III)-PLTMBH complex (fig. 2a) showed 15978cm^{-1} $6A_{1g} \rightarrow 4T_{1g}(G)$, 23746cm^{-1} $16A_{1g} \rightarrow 4A_{1g}$, $4E_g(G)$, 29533cm^{-1} $16A_{1g} \rightarrow 4E_g(D)$ and 31327cm^{-1} $6A_{1g} \rightarrow 4T_{1g}(P)$ transitions, suggesting high spin octahedral geometry for the complex. The band at 36764cm^{-1} is a result of the CT transition.

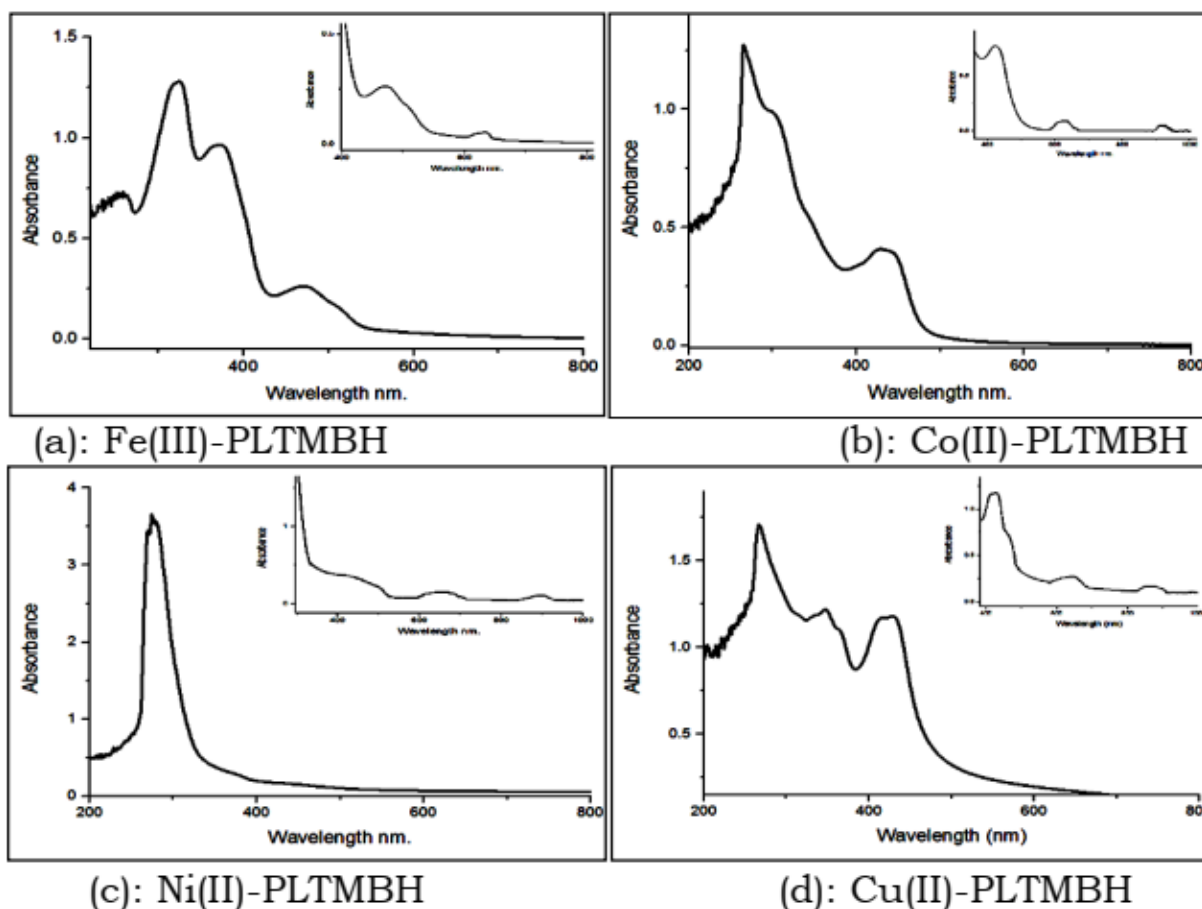


Fig.2(a-d): Electronic spectra of metal complexes of PLTMBH

The UV-visible spectrum of the Co(II)-PLTMBH complex revealed d-d transitions at $4T_{1g}(F)4T_{2g}(F)$ (11952cm^{-1}), $4T_{1g}(F)4A_{2g}(F)$ (15898cm^{-1}) and $4T_{1g}(F)4T_{1g}(P)$ (23148cm^{-1}), indicating an octahedral geometry. The band 37453cm^{-1} corresponds to a CT transition.

The Ni(II)-PLTMBH complex exhibited three d-d transitions in its UV-visible spectrum at $11358\text{cm}^{-1}3A_{2g}3T_{2g}(F)$, $15822\text{cm}^{-1}3A_{2g}3T_{1g}(F)$, and $22371\text{cm}^{-1}3A_{2g}3T_{1g}(P)$, indicating an octahedral geometry. The band at 36363cm^{-1} could be the result of CT transition.

The d-d transitions $2B_{1g}2A_{1g}$ (11862cm^{-1}), $2B_{1g}2B_{2g}$ (16749cm^{-1}) and $2B_{1g}2E_{1g}$ (24135cm^{-1}) in the electronic spectrum of the Cu(II)-PLTMBH complex indicate a distorted octahedral geometry for the complex. The width of the bands is indicative of Jahn Teller's distortion. The band at 37452cm^{-1} corresponds to the CT transition. Includes insets depicting the d-d transitions of the complexes.

4. CONCLUSION:

Spectro-analytical techniques such as elemental analysis, magnetic susceptibility measurements, molar conductance, TGA, IR, $^1\text{H-NMR}$, UV-visible, LC-MS, and ESR spectral analyses were used to characterize the synthesized complexes. Analytical and spectroscopic data indicate that the ligands PLHBH, PLNBH, PLDCBH, PLFBH, and PLTMBH function as tridentate O,N,O donors and are coordinated to the metal ions via phenolic-O, azomethine-N, and carbonyl-O atoms. For all ligands, octahedral geometry was postulated for the Fe(III), Co(II), Ni(II), Cu(II), Zn(II), and Cd(II) complexes. Except for Zn(II)-PLFBH and Co(II)-PLTMBH, which formed 1:1 (ML) complexes, all other complexes have formed in the 1:2 ratio (ML₂). The condensation products of primary amines with carbonyl substances like ketones and aldehydes are the schiff bases. These compounds all share the imine (C=N) group, often known as azomethine, as a structural component. According to studies, the biological activity of schiff bases is caused by the presence of a lone pair of electrons in the nitrogen atom of the imine group. In the schiff base family of chemical compounds, hydrazones of ketones and aldehydes have the structural formula $\text{R}_1\text{R}_2\text{C}=\text{NNH}_2$ [10]. It is known that aryl, acyl, and heteroaryl compounds' hydrazoneschiff bases feature an extra donor site, C=O, which increases their adaptability and flexibility. When another functional group, such as a -OH, -NH, or -SH, is present near to the azomethine group, these compounds operate as good chelating agents, creating a five- or six-membered ring with the metal ion. Because of their wide range of pharmacopoeial actions, hydrazone moieties have been significant. By forming stable chelates with the transition

metal ions that catalyze physiological processes, hydrazones also demonstrate antituberculosis activity. Numerous biological applications can be made of the metal complexes of hydrazone ligands, particularly those containing oxygen and nitrogen. The domains of bioinorganic chemistry, supramolecular chemistry, biomedical applications, catalysis, and material science have all greatly enlarged the coordination chemistry of hydrazones.

5. REFERENCES

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