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Transition Metal Complexes of HMA-GPA Schiff Base Synthesis Characterization and Antimicrobial Activity

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ABSTRACT

A Schiff base ligand, HMA-GPA, synthesized from 2-hydroxy-3-methoxybenzaldehyde and L-arginine, and its Cu(II), Ni(II), and Co(II) complexes were investigated by elemental analysis, infrared spectroscopy, thermal analysis, electron spin resonance (ESR), scanning electron microscopy (SEM), and antimicrobial screening. The analytical data support a 1:1 metal-to-ligand stoichiometry for the synthesized complexes. Infrared spectral changes, particularly the shifts of the azomethine, phenolic C–O, and carboxylate bands, indicate coordination through azomethine nitrogen, phenolic oxygen, and carboxylate oxygen, giving a tridentate coordination mode. Electronic spectral and magnetic susceptibility results support square-planar geometries for the Cu(II) and Ni(II) complexes and an octahedral geometry for the Co(II) complex. The complexes also exhibit electrolytic behavior, while ESR measurements further support the square-planar configuration of the Cu(II) complex. Thermal studies show initial loss of crystallized water followed by decomposition of coordinated ligand species. SEM examination reveals distinct morphological features for the three metal complexes. The results indicate that HMA-GPA forms stable coordination compounds with different structural and biological characteristics.

Keywords— Schiff base, HMA-GPA, L-arginine, 2-hydroxy-3-methoxybenzaldehyde, Cu(II), Ni(II), Co(II), spectral characterization, thermal analysis, ESR, antimicrobial activity

INTRODUCTION

Transition-metal coordination compounds occupy an important position in biological and medicinal chemistry. The supplied chapter emphasizes that first-row transition-metal ions occur in physiological systems and that imbalance in metal-ion ratios may be associated with disease[1]. Coordination chemistry therefore provides a route for studying metal–ligand interactions and for exploring metal complexes with potential biological applications. Amino acids participate in numerous biological processes, while Schiff bases containing nitrogen and oxygen donor atoms can coordinate metal ions in monodentate, bidentate, chelating, or bridging modes [2]. Carboxylate-containing ligands are especially relevant because their oxygen atoms provide flexible coordination sites[3]. L-Arginine is highlighted as a biologically important amino acid with roles in cell division and immune functioning. Its guanidine functionality and ability to participate in coordination chemistry make it a useful precursor for Schiff-base ligand synthesis. In the present work, L-arginine was reacted with 2-hydroxy-3-methoxybenzaldehyde to obtain the Schiff base HMA-GPA[4], followed by preparation of Cu(II), Ni(II), and Co(II) complexes. The objective of this paper is to consolidate the synthesis, analytical characterization, structural interpretation, thermal behavior, morphology, and antimicrobial observations reported

2.EXPERIMENTAL OVERVIEW

The synthesis of ligand L1 (HMA-GPA) and the corresponding Cu(II), Ni(II), and Co(II) complexes was carried out by condensation of aprimary aminewith an 2-hydroxy-3-methoxybenzaldehyde For L-arginine, the amino group can participate in condensation with the aldehyde[5]. The analytical and spectral techniques were likewise introduced previously. Accordingly, this paper retains the reported characterization results and focuses on their integrated interpretation rather than reconstructing experimental conditions obtained from 2-hydroxy-3-methoxybenzaldehyde and L-arginine. The metal complexes were prepared with Cu(II), Ni(II), and Co(II), and the analytical data indicated a 1:1 metal-to-ligand stoichiometric relationship. The compounds were reported to be soluble in ethanol, DMSO, and DMF, with the ligand slightly soluble in water

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3.CHARACTERIZATION OF THE SCHIFF BASE LIGAND

A. Infrared Spectroscopy

The IR spectrum of HMA-GPA contains a broad band at 3429 cm^{-1} assigned in the source to O–H stretching associated with coordinated water, a sharp band at 1638 cm^{-1} attributed to the azomethine ν(CH=N) vibration, and carboxylate bands at 1599 and 1351 cm^{-1} corresponding to asymmetric and symmetric COO^- stretching. The phenolic C–O stretching vibration occurs at 1231 cm^{-1}[6]. These bands provide the principal diagnostic features used for comparison with the metal complexes.

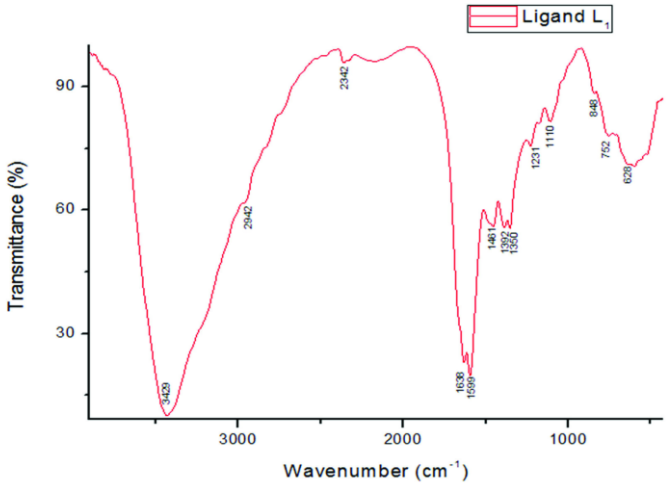


Fig. 1. IR spectrum of Schiff base ligand L1 (HMA-GPA).

4.. SPECTRAL CHARACTERIZATION OF METAL COMPLEXES

A. Cu(II) Complex

For the Cu(II) complex, the azomethine band shifts from 1638 to 1628 cm^{-1}, indicating involvement of the azomethine nitrogen in coordination. The broad O–H band at 3446 cm^{-1} and additional bands at 840 and 997 cm^{-1} are associated with water molecules. The phenolic C–O band shifts to 1224 cm^{-1}. The asymmetric and symmetric carboxylate bands occur at 1587 and 1364 cm^{-1}; their separation of 223 cm^{-1} is interpreted in the source as evidence for monodentate carboxylate coordination. New bands at 603 and 461 cm^{-1} are assigned to Cu–O and Cu–N vibrations.

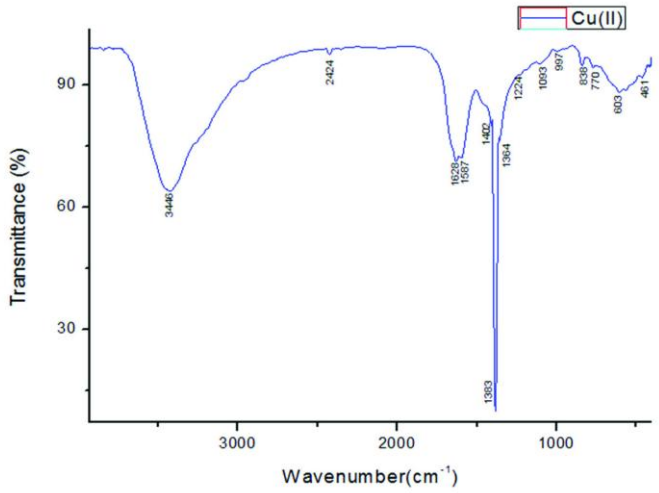


Fig. 2. IR spectrum of Cu(II) complex [Cu(L1)(H2O)](NO3)2·4H2O.

B. Ni(II) Complex

The Ni(II) complex shows the azomethine vibration at 1626 cm^{-1}. The phenolic C–O, asymmetric COO^-, and symmetric COO^- bands are observed at 1219, 1589, and 1360 cm^{-1}, respectively. The difference between the carboxylate stretching frequencies is 229 cm^{-1}, again assigned to monodentate carboxylate coordination [7]. Bands at 555 and 485 cm^{-1} are attributed to Ni–O and Ni–N vibrations.

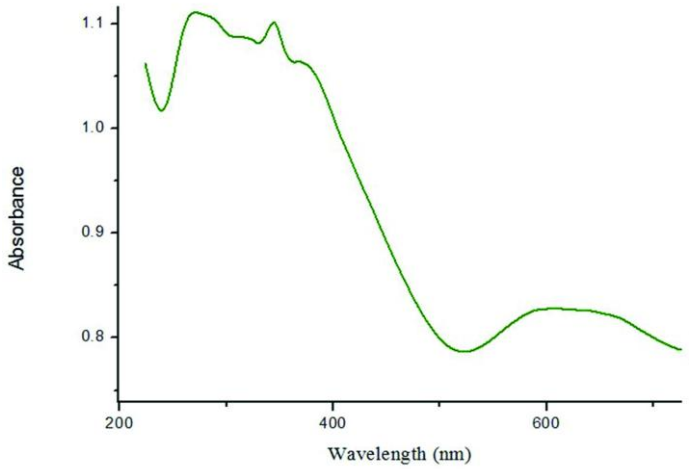


Fig. 3. UV–Vis spectrum of Ni(II) complex [Ni(L1)(H2O)](NO3)2·H2O.

C. Co(II) Complex

For the Co(II) complex, the ν(CH=N) band occurs at 1630 cm^{-1}. Carboxylate bands at 1585 and 1365 cm^{-1} give a separation of 220 cm^{-1}, which is interpreted as monodentate coordination. The phenolic C–O band shifts to 1208 cm^{-1}. New bands at 550 and 481 cm^{-1} are assigned to Co–O and Co–N vibrations. The data collectively support coordination through azomethine nitrogen and oxygen donor sites.

5.. ELECTRONIC SPECTRA

The ligand exhibits bands at 272 and 347 nm, assigned to π–π* and n–π* transitions, respectively. In the Cu(II) complex, corresponding bands occur at 273 and 356 nm, together with a broad d–d absorption in the 580–640 nm region[8]. The source assigns the Cu(II) complex to a square-planar environment with a magnetic moment of 1.90 BM.

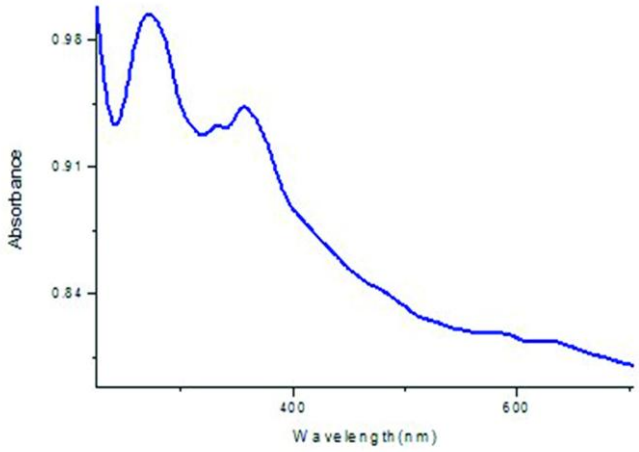


Fig. 4. UV–Vis spectrum of Cu(II) complex [Cu(L1)(H2O)](NO3)2·4H2O.

The Ni(II) complex shows absorptions at 282 and 373 nm due to π–π* and n–π* transitions and a d–d band at 622 nm. This is interpreted as supporting a distorted square-planar geometry and diamagnetism. The Co(II) complex shows bands at 284 and 378 nm, together with d–d transitions around 500, 700, and 803 nm, consistent in the source with a high-spin octahedral environment and a magnetic moment of 4.93 BM [9].

6. THERMAL ANALYSIS

Thermal analysis was performed from approximately ambient temperature to 800–850 °C under nitrogen at a controlled heating rate of about 10 °C min^{-1}. The Cu(II) complex initially loses four lattice water molecules between 30 and 100 °C, followed by further dehydration and decomposition of nitrate and ligand fragments[10]. Above about 730 °C, CuO residue formation begins.

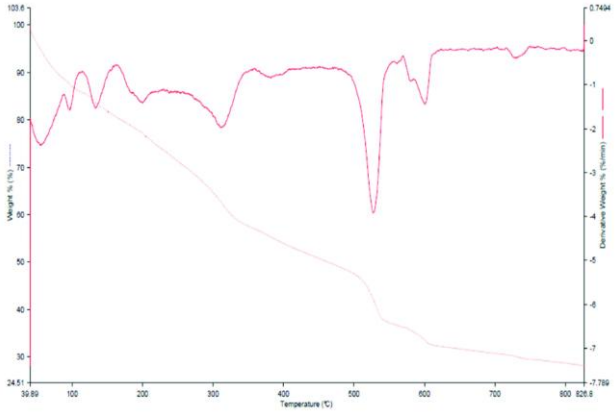


Fig. 5. Representative thermal analysis image for the Cu(II) complex.

7. ESR SPECTRUM OF CU(II) COMPLEX

The ESR spectrum of the Cu(II) complex was recorded in the crystalline state at 298 K in the X-band using DPPH as the reference. The reported g∥ and g⊥ values are 2.20 and 2.06, respectively[11], satisfying g∥ > g⊥ > ge and indicating that the unpaired electron occupies the dx^2-y^2 orbital. The source interprets the g∥/A∥ ratio of 110 and the bonding parameter G of 5 as supportive of square-planar stereochemistry and the absence of exchange interaction between Cu(II) centers.

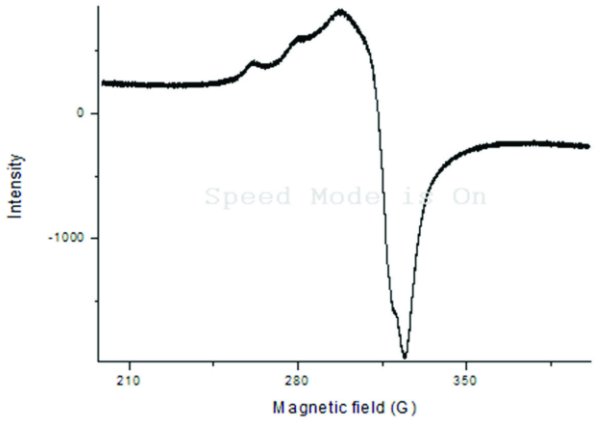


Fig. 6. ESR spectrum of Cu(II) complex [Cu(L1)(H2O)](NO3)2·4H2O.

8. MORPHOLOGICAL CHARACTERIZATION

A. Scanning Electron Microscopy

SEM analysis was used to examine the morphological features of the Cu(II), Ni(II), and Co(II) complexes. The source reports relatively uniform matrices with defined boundaries for all three complexes[12]. At lower magnification, the Cu(II) complex is described as needle-shaped and flower-like, while higher magnification reveals elongated grass-like features and a smooth surface without obvious voids.

The Ni(II) complex appears as a crystalline mass with an algae-like morphology at lower magnification and irregular broken-ice-like structures at higher magnification. The Co(II) complex is described as a compact rocky mass at lower magnification and as clusters of cotton-like features at higher magnification. The absence of visible voids and cracks is interpreted in the source as supporting the occurrence of complexation. Differences among the micrographs are attributed to the identity of the coordinated metal ion.

9.DISCUSSION

The combined characterization results provide a consistent picture of HMA-GPA coordination chemistry. The shift of the azomethine ν(CH=N) band to lower wavenumber after complexation, movement of the phenolic C–O band, and characteristic carboxylate separations are the principal IR indicators used to establish metal binding. New low-frequency M–O and M–N bands further support coordination through nitrogen and oxygen donor sites. Electronic spectra and magnetic susceptibility measurements differentiate the coordination environments of the three metal ions. The Cu(II) complex is associated with square-planar geometry and a 1.90 BM magnetic moment;

the Ni(II) complex is reported as diamagnetic and distorted square planar; and the Co(II) complex is assigned an octahedral environment with a 4.93 BM magnetic moment. ESR data independently reinforce the square-planar interpretation for Cu(II).

Thermal analysis provides complementary evidence for the number and type of water molecules and the decomposition sequence of the complexes. The progressive loss of lattice and coordinated water followed by nitrate and ligand decomposition is consistent with the formulations proposed in the source. SEM observations demonstrate that the morphology changes with the metal ion, even though the same Schiff base ligand is used.

10.CONCLUSION

HMA-GPA was synthesized from 2-hydroxy-3-methoxybenzaldehyde and L-arginine and investigated together with its Cu(II), Ni(II), and Co(II) complexes. IR, electronic spectroscopy, ^{1}H NMR, magnetic susceptibility, thermal analysis, ESR, and SEM results collectively support coordination through azomethine nitrogen, phenolic oxygen, and carboxylate oxygen. Cu(II) and Ni(II) are assigned square-planar environments, whereas Co(II) is assigned an octahedral environment. The antimicrobial screening demonstrates distinct activity profiles for the ligand and each metal complex. The study therefore establishes a coherent relationship between spectral characterization, proposed coordination geometry, thermal behavior, morphology, and biological screening for this HMA-GPA metal-complex system.

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