



Synthesis and Spectral Studies Of Polypyridine Complexes Supported by Schiff-Base Ligands Derived From 2-Chloro Ethyl Amine

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Abstract

Polypyridine complexes $[M(\text{phen})_2(L)](\text{OAc})_2 \cdot (n\text{H}_2\text{O})$ **1-3**, (L = ligands derived from 2-chloro ethyl amine and ortho hydroxy benzaldehydes have been synthesized from the reaction of the metal precursor complex $[M(\text{phen})_2](\text{OAc})_2 \cdot 6\text{H}_2\text{O}$ with the respective ligands in ethanol and water. The ligands and complexes have been characterized with the aid of elemental analysis and FT-IR, FAB-Mass, UV-Vis., ¹H-NMR, ESR spectroscopic methods and further analyzed by powder XRD and thermal studies. Elemental analysis data confirmed that the complexes have a 1:2:1 molar ratio among the metal and ligands. FT-IR and ¹H-NMR spectral studies indicate the ligands are bidentate and the binding sites are azomethine nitrogen and phenolic oxygen atoms. Powder XRD shows the sharp crystalline peaks indicating the crystalline state of the complexes. Thermal decomposition profiles are consistent with the proposed formulations.

Keywords: 2-chloro ethyl amine, 1, 10-phenanthroline, Polypyridine complexes.

1. Introduction

Schiff base containing nitrogen and oxygen donor atoms and their transition metal complexes play an important role in inorganic research due to their unique coordinative and pharmaceutical properties¹⁻⁵. They have been extensively studied in great details for their various crystallographic, structural and magnetic features^{6,7}. Among these, polypyridine complexes of Schiff base ligands do have significant interest because of their excellent chemical, electrochemical and photochemical properties as well as potential biological applications such as antitumor,

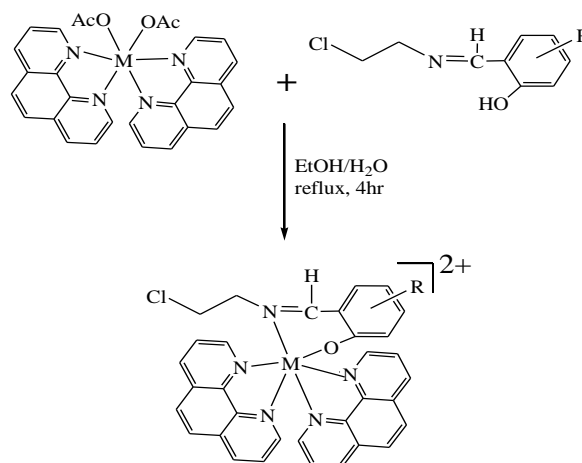
anticandida, antimycobacterial and antimicrobial activities⁸⁻¹⁰. Furthermore, the interaction of these complexes with DNA has gained much attention due to their possible applications as new therapeutic agents¹¹⁻¹³. This prompted us to synthesize new Schiff base ligands derived from 2-chloro ethyl amine and their three new Co(II) and Ni(II) polypyridine complexes. They were characterized using analytical and various spectral techniques.

2. Experimental

Synthesis of complexes: Metal precursor $[M(\text{phen})_2](\text{OAc})_2 \cdot 6\text{H}_2\text{O}$ was used as starting

material to synthesize all the new complexes 1–3. The complexes were prepared by refluxing a solution of $[M(\text{phen})_2](\text{OAc})_2 \cdot 6\text{H}_2\text{O}$ and ligands (1 mmols) in aqueous

ethanol (20 ml) for 4h. The solid obtained were filtered, washed with ethanol and then dried as shown in (Scheme 1).



Scheme 1. Outline the synthesis of complexes (1-3).

3. Results and discussion

Elemental Analysis: Elemental analysis data confirmed that the complexes have a 1:2:1 molar ratio between the metal and ligands. i.e. one mole of metal acetate reacted with two moles of 1,10-phenanthroline and one mole of ligands to give the corresponding complexes 1/2/3. All the complexes show the analytical results close to the theoretical values indicating the presence of two types of ligands.

IR Spectra: The IR spectra of ligands L^1 and L^2 and their complexes 1 and 2 are shown in (Figures 1 and 2). The spectra of free Schiff base ligands L^1 , L^2 and L^3 showed the broad bands at 3444 cm^{-1} were due to stretching vibrations of phenolic OH¹⁵⁻¹⁷. These bands were absent in all the complexes, indicating deprotonation on coordination of the Schiff base ligands to metal ion. In addition, the bands at 1346 cm^{-1} attributed to the phenolic C–O stretching vibrations of the free ligands were blue-shifted to 1426 cm^{-1} upon complexation suggesting the involvement of the phenolic oxygen atom in the

coordination¹⁸⁻²⁰. The imine (C=N) functional group of the free ligands was observed as strong bands between $1670\text{--}1643\text{ cm}^{-1}$ were red-shifted to $1625\text{--}1586\text{ cm}^{-1}$ in the spectra of the complexes, indicating coordination of azomethine nitrogen of the Schiff base ligands to metal ion²¹⁻²³. Thus it can be concluded that the schiff bases are bidentate, coordinating via phenolic O and the azomethine N. Furthermore, the infrared spectra of free Schiff base ligands showed the bands at 3070 cm^{-1} and 2877 cm^{-1} were due to the stretching vibrations of (C–H) and (CH₂). The bands observed at 1296 cm^{-1} and 632 cm^{-1} were due to the stretching vibrations of (C–N) and (C–Cl)^{24,25}. These bands were shifted to negative frequencies after complexations. The presence of water molecules in the complexes was indicated by broad absorption bands at 3400 cm^{-1} . The mode of coordination of the Schiff base ligands was further supported by the appearance of two new weak bands in the lower frequency region at $570\text{--}520\text{ cm}^{-1}$ and $423\text{--}416\text{ cm}^{-1}$. These bands were assigned to the M–N and M–O stretching vibrations, respectively^{17,18}.

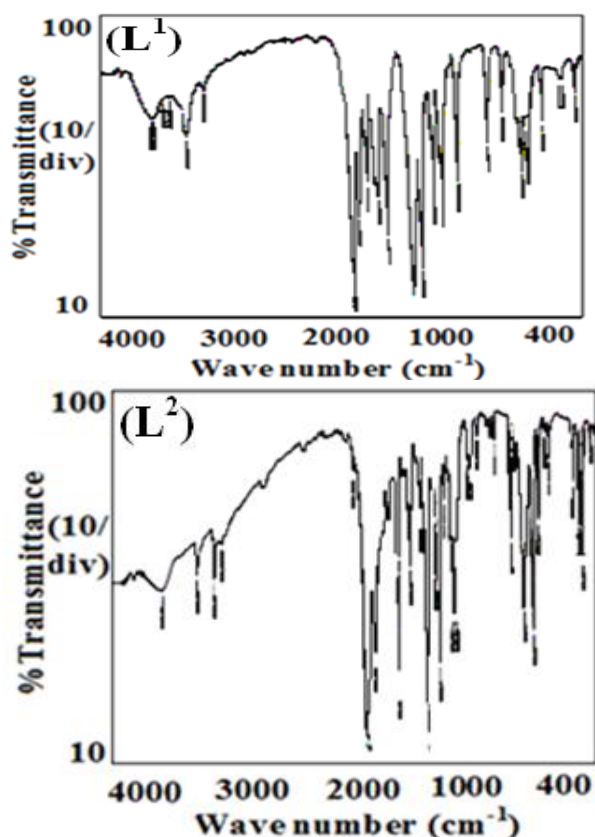


Figure 1. IR spectra of the ligands (L^1) and (L^2).

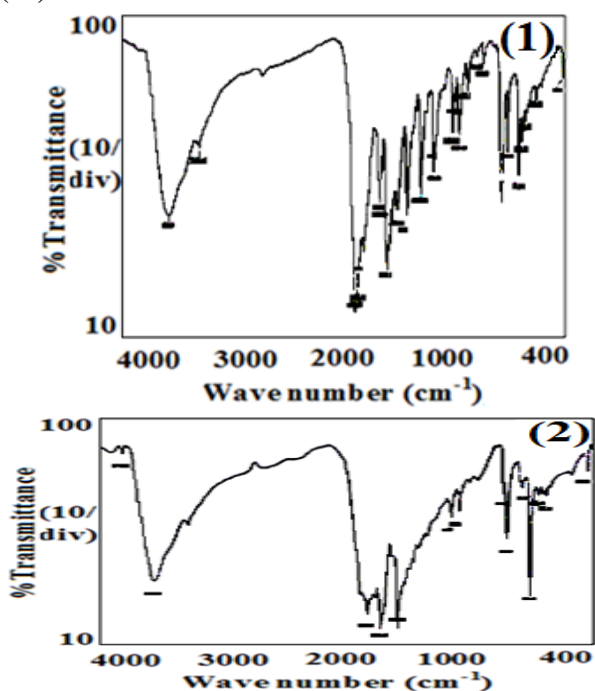


Figure 2. IR spectra of the complexes (1,2)

Electronic Spectra: The electronic spectra of the ligands and their complexes were carried out in DMSO. Three absorption bands were observed in the electronic spectra of the free Schiff base ligands L^1 , L^2 and L^3 in the 264–430 nm, 264–435 nm and 261–434 nm range respectively were assigned to π - π^* and n - π^* transitions. The bands observed at 350 nm, 316 nm and 349 nm were assigned to the π - π^* transitions of the azomethine, which were shifted to 414 nm, 412 nm and 437 nm in the electronic spectra of complexes 1–3 respectively indicating the azomethine nitrogen was involved in coordination^{20,21}. The bands observed at 264 nm were assigned to the π - π^* transitions of the phenol²⁵. The absorption bands at about 270 nm were originated from π - π^* transitions of phenanthroline ring in all the complexes^{16,17}. The electronic spectra of complexes 1, 2 and 3 exhibited three well defined bands in the 250–414, 270–450 and 265–437 nm range respectively were assigned to intra-ligand charge transfer transitions. The positions of these bands suggested an octahedral environment around metal atom^{26,27}. The weak absorption bands in the spectra of complexes were contribution from spin allowed metal to ligand charge transfer, MLCT²⁰.

Powder XRD: Powder XRD patterns of complexes show the sharp crystalline peaks indicating their crystalline phase. The diffraction pattern of complexes 2 and 3 is measured in the range ($2\theta = 0$ – 80°) are shown in (Figure 3).

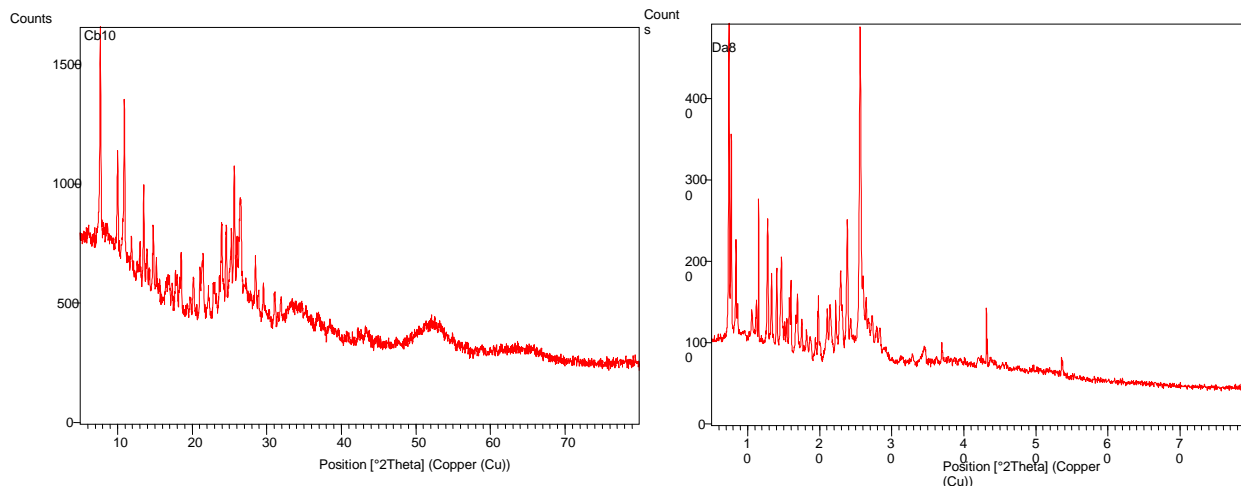


Figure 3. Powder XRD patterns of complexes (2) and (3).

Thermogravimetric study:
Thermogravimetric curves for the complexes are shown in (Figure 4) and their thermal stability data are listed in (Table 1). Thermal

decomposition curves of the complexes 1 and 3 showed a sequence of three decomposition steps, unlike complex 2 showed four decomposition steps²⁸⁻³⁰.

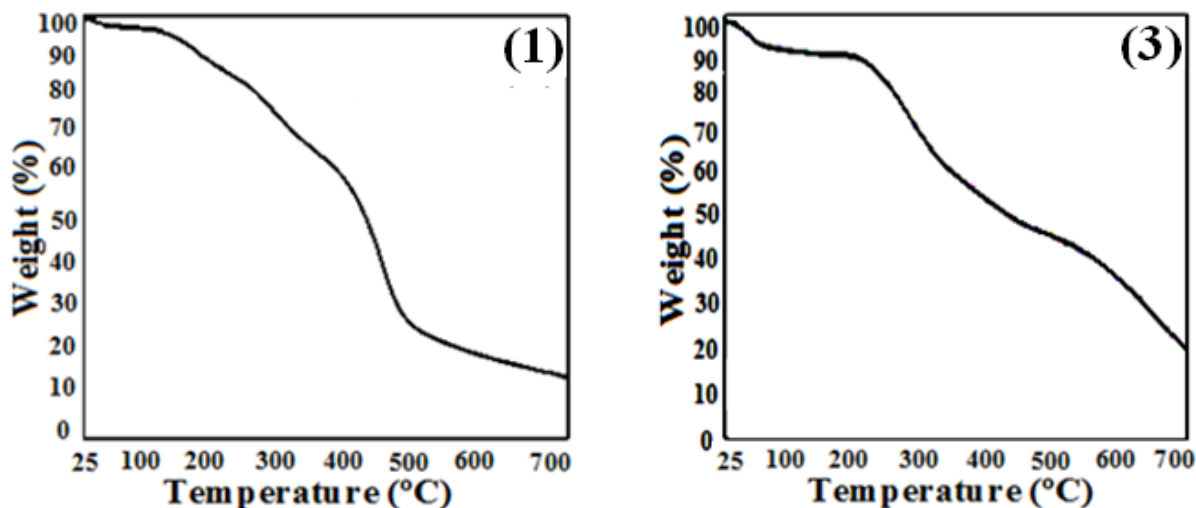


Figure 4. TGA curves of the complexes (1) and (3).

4. Conclusions

Polypyridine complexes supported by Schiff base ligands derived from 2-chloro ethyl amine were synthesized and characterized. Based on the above observations of the elemental analysis, UV-Vis., IR, ¹H-NMR, ESR spectral data it is possible to determine the type of coordination

of the ligands in their complexes. The spectral data reveal that all the complexes were six coordinated and possess octahedral geometry around the metal ion. Powder XRD indicates the crystalline state of the complexes. Thermal property measurements show that the complexes have good thermal stability.



5. References

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