

Chemical Preparation, Spectro-Magnetic and Biocidal Studies on Some Divalent Transition Metal Complexes of Schiff's Base Derived from 1-Phenyl-2-(Pyridin-2-yl)ethane-1,2-dione and Ethylenediamine

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Abstract

The tetra-dentate Schiff's base ligand, N, N-di(pyridin-2-ylbenzenoylmethylene)ethylenediamine and its complexes of divalent transition metals like Ni(II), Co(II), Cu(II) and Zn(II) were investigated in terms of synthesis, elemental analysis, molar conductivity, infrared spectra, ultraviolet-visible (electronic spectra) and magnetic susceptibility measurements. The ligands have been synthesized by condensation of 1-phenyl-2-(pyridin-2-yl) ethane-1, 2-dione and ethylenediamine. Each divalent transition metal complexes possess eight coordinate octahedral geometrical structures. Bactericidal and fungicidal activities of the compounds were evaluated in vitro by disc diffusion method. Antimicrobial studies conducted on two bacteria and two fungi revealed higher antimicrobial activities by complexes than the Schiff base ligand against all the microbes used.

Keywords: Biocidal activity; 1-phenyl-2-(pyridin-2-yl)ethane-1,2-dione; Tetra-dentate ligand; Schiff's bases

Introduction

Ligand, a metal surrounded by a cluster of ions or molecule, is used for preparation of complex compounds named as Schiff's bases [1]. Tetra-dentate Schiff's bases are well known for their coordination with various metal ions, forming stable compounds [2-4]. Schiff's bases with O and N donor binding sites have attracted considerable attention because of their preparative accessibility, potential biological properties [3-8] applications in industries as dyes [3] and versatile coordination properties leading to formation of stable complexes with transition metal ions in unusual coordination numbers and isomeric structures [4-7]. Schiff's bases have been widely used in many fields e.g., biological, inorganic, analytical and drug synthesis, as bi-dentate ligands in the field of coordination chemistry [2]. The multifarious biological including anti-pathogenic behavior of these metal-Schiff's base complexes is of paramount importance for designing metal-based drugs. In view of mentioned distinguished features of these compounds we report here the synthesis, magnetic, spectral and antimicrobial

studies of some divalent first series transition metals like Ni(II), Co(II), Cu(II) and Zn(II) complexes with the novel Schiff's base ligand, N,N-di(pyridin-2-ylbenzenoylmethylene)ethylenediamine, which is derived from the condensation reaction of 1-Phenyl-2-(Pyridin-2-yl)ethane-1,2-dione and ethylenediamine.

Experimental

1-phenyl-2-(pyridin-2-yl) ethane-1,2-dione, precursor of the ligand was prepared by the oxidation of 1-phenyl-2-(pyridin-2-yl)propan-1-one (0.5 mol) with SeO_2 (0.5 mol) [4] in 95% alcohol followed by refluxing for 2 h (Figure 1). Refluxed reaction mixture was allowed to stand to cool and yellow brown solution was decanted, filtered concentrated over water bath [9]. Concentrated reaction mixture was finally dissolved in ethoxyethane and filtered to remove selenium, if any, from the product and dried in air (Figure 1).

The Schiff's base ligand, N, N-di (pyridin-2-ylbenzenoylmethylene) ethylenediamine (L) was synthesized by the condensation of ethylenediamine and 1-phenyl-2-(pyridin-2-yl) ethane-1, 2-dione (1: 2 molar ratio), dissolved in ethanol (Figures 2 and 3). The resulting reaction mixture was refluxed for ≈ 1 h. The yellow solid precipitate of Schiff base obtained was filtered, washed with distilled water dried, recrystallized from ethanol and finally preserved in a desiccator. Yield: 41% (melting points: $\approx 212^\circ\text{C}$) [10].

An ethanolic (10 ml) solution of Schiff's base ligand (10 mM) was mixed with metal (II) chloride (5 mM) in ethanol (10 ml) solution keeping ligand-metal ratio 1:1 followed by few drops of acetic acid (pH = 6). The mixture was then refluxed for ≈ 1.5 h on a water bath till the complex precipitated out. Precipitate obtained was dried over KOH

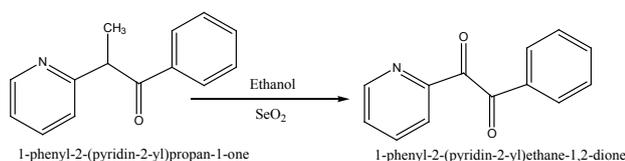


Figure 1: Preparation of 1-phenyl-2-(pyridin-2-yl)ethane-1,2-dione from 1-phenyl-2-(pyridin-2-yl)propan-1-one.

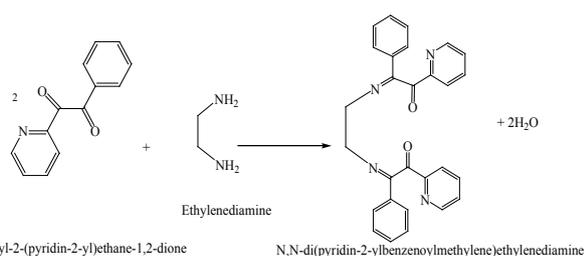


Figure 2: Preparation of N,N-di(pyridin-2-ylbenzenoylmethylene) ethylenediamine, Schiff's Base Ligand.

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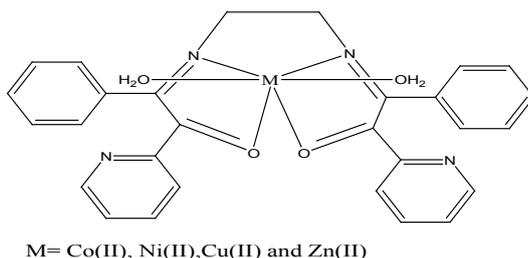


Figure 3: Divalent transition metal complexes with N, N-di (pyridin-2-ylbenzenoylmethylene) ethylenediamine ligand

| S. No. | Compounds | Mol. Wt. (g mol ⁻¹) | Color | Yield (%) | M.P (°C) | Molar Cond. (Ω ⁻¹ cm ² mol ⁻¹) | μ _{eff} (B.M.) | Elemental analysis (%) | | | |
|--------|---|---------------------------------|--------------|-----------|----------|--|-------------------------|------------------------|----------------|------------------|------------------|
| | | | | | | | | Calculated. (Found) | | | |
| | | | | | | | | C | H | N | M |
| 1 | C ₂₈ H ₂₂ N ₄ O ₂ (L) | 446.51 | Yellow | 41 | 212 ± 2 | - | - | 75.25 (67.01) | 4.93 (4.62) | 12.54 (8.43) | - |
| 2 | [Co (C ₂₈ H ₂₂ N ₄ O ₂)(H ₂ O) ₂] | 541.44 | Brown yellow | 64 | >300 | 13.7 | 2.25 | 62.06 (64.02) | 4.06 (4.88) | 10.34 (12.06) | 10.88 (12.56) |
| 3 | [Ni (C ₂₈ H ₂₂ N ₄ O ₂)(H ₂ O) ₂] | 541.20 | Black green | 58 | 298 ± 2 | 20.4 | 3.23 | 62.08 (63.55) | 4.07 (3.98) | 10.35 (11.02) | 10.84 (11.27) |
| 4 | [Cu (C ₂₈ H ₂₂ N ₄ O ₂)(H ₂ O) ₂] | 546.06 | Green brown | 42 | 281 ± 2 | 14.5 | 2.19 | 61.53 (63.13) | 4.03 (4.49) | 10.25 (10.42) | 11.64 (12.10) |
| 5 | [Zn (C ₂₈ H ₂₂ N ₄ O ₂)(H ₂ O) ₂] | 547.92 | Light yellow | 45 | >300 | 11.2 | Diamag. | 61.32 (62.45) | 4.01 (3.89) | 10.22 (11.78) | 11.94 (11.02) |

L = Schiff's base ligand

Table 1: Analytical data, magnetic moment and physical properties of compounds.

pellets. The solid product obtained was filtered, washed with distilled water and dried in vacuum. The purity of the compounds was tested by TLC on silica gel layers using chloroform, acetone and methanol solvents [9].

The in-vitro microbial screening of the compounds (Schiff's base ligand and their metal complexes) was tested against two bacteria species (*Escherichia coli* and *Staphylococcus aureus*) and two fungi species (*Aspergillus niger* and *Colletotrichum gloeosporioides*) by disc diffusion method [8].

Melting points were determined in open glass capillaries with Stuart SMP-10 melting point apparatus and are uncorrected. Microanalyses were performed on a Vario EL-III analyzer. IR spectra were recorded on Shimadzu Prestize-21 FT-IR spectrophotometer in 4000-200 cm⁻¹ region in KBr medium. The electronic spectra were recorded on SP65 UV-Visible spectrophotometer in methanol solvent. Magnetic susceptibility was measured at room temperature (295°C) on MSB-Auto (Sherwood Scientific Ltd) balance. The molar conductance of complexes was measured in methanol at room temperature on Jenway digital conductivity bridge. Metal contents of the complexes were determined by atomic absorption spectroscopy using BUCK Scientific spectrophotometer.

Results and Discussion

The analytical data along with some physical properties of the complexes are summarized in table 1. The Schiff's base ligand L, on interaction with Cu(II), Co(II), Ni(II) and Zn(II) chlorides, gives up complexes corresponding to the general formula [ML(H₂O)₂]. The analytical data shows that the metal to ligand ratio is 1:1. They are soluble in ordinary organic solvents. The low molar conductivity (Λ_m) values of the complexes in DMF reveal their non-electrolytic nature [10,11].

In order to identify the binding modes of the ligand in the complexes, IR spectrum of the free ligand was compared with that of complexes.

The free ligand displayed νC=N and νC=O bands at 3458 cm⁻¹ and 1166 & 1229 cm⁻¹ of the groups. In the spectra of the complexes, lowering in frequency of νC=O bands (ca. 1045 & ca. 1103 cm⁻¹) and appearance of a new band in 488-561 cm⁻¹ attributed to νM-O reveal the bands that occur in the low wavenumbers range were assigned to the stretching vibrations ν(M-O) coordination of the ligand [12].

The band(s) at 1605-1630 cm⁻¹ due to the azomethine group of the Schiff's base ligand underwent a shift to lower frequency (1570-1600 cm⁻¹) after complex formation, indicating the coordination of azomethine nitrogen to metal atom and this can be explained by the donation of electrons from nitrogen to the empty d-orbitals of the metal atom. In the spectra of all complexes, the broad band at ≈3300 cm⁻¹, collectively with new band at 880 cm⁻¹ indicating the presence of coordinated water. The nature of metal-ligand bonding is confirmed by the newly formed band at 501 cm⁻¹ in the spectra of the complexes which is tentatively assigned to M-N vibration [5,9].

The magnetic moment value of Cu(II) complex is 2.25 BM which calls to mind a distorted octahedral geometry [10] around the metal ion. The magnetic moment of Co(II) complex is 3.23 BM which suggests the high spin hexa-coordinated octahedral arrangement of ligand molecules around the metal ion. The Ni(II) complex has magnetic moment value of 2.19 BM signifying a spin-free octahedral configuration [11]. The Zn(II) complex is found to be diamagnetic as expected for d10 configuration [2].

The UV-Vis spectroscopic (electronic spectral) studies of the Schiff's base Ligand Complexes of Co(II), Ni(II), Cu(II) and Zn(II) were carried out in DMSO solution. The absorption spectrum of the Co(II) complex shows bands at ε ~ 20 L mol⁻¹ cm⁻¹ and ε ~ 50 L mol⁻¹ cm⁻¹ attributed to ⁴T_{1g}(F) → ⁴T_{2g}(F) and ⁴T_{1g}(F) → ⁴T_{1g}(P) transitions respectively in an octahedral field [13]. The spectral parameters of Co (II) complex are as follows [14]: Dq = 1036.8 cm⁻¹, B = 715.04 cm⁻¹, β = 0.736 and β₀ = 26.4 %. The reduction of Racah parameter from the free ion value 971 cm⁻¹ and β₀ value of 26.4% testifies the presence of considerable covalence

| S.No | Compounds | Inhibition Zone (mm) | | | | | | | |
|------|---|----------------------|-------|------------------|-------|--------------------------|-------|-----------------|-------|
| | | <i>E. coli</i> | | <i>S. aureus</i> | | <i>C.gloeosporioides</i> | | <i>A. niger</i> | |
| | | 10 µl | 20 µl | 10 µl | 20 µl | 10 µl | 20 µl | 10 µl | 20 µl |
| 1 | C ₂₈ H ₂₂ N ₄ O ₂ (L) | 7 | 9 | - | 9 | - | - | 7 | 10 |
| 2 | [Co (C ₂₈ H ₂₂ N ₄ O ₂)(H ₂ O) ₂] | 15 | 18 | 13 | 22 | 15 | 20 | 15 | 22 |
| 3 | [Ni (C ₂₈ H ₂₂ N ₄ O ₂)(H ₂ O) ₂] | 17 | 19 | 25 | 31 | 13 | 20 | 8 | 25 |
| 4 | [Cu (C ₂₈ H ₂₂ N ₄ O ₂)(H ₂ O) ₂] | 17 | 20 | 22 | 27 | 8 | 12 | 10 | 15 |
| 5 | [Zn (C ₂₈ H ₂₂ N ₄ O ₂)(H ₂ O) ₂] | 18 | 20 | 21 | 28 | 10 | 13 | 11 | 25 |
| 6 | DMSO (Control) | - | - | - | - | - | - | - | - |
| 7 | <i>Chloramphenicol</i> | 21 | 23 | 25 | 30 | - | - | - | - |
| 8 | <i>Bavistin</i> | - | - | - | - | 15 | 20 | 20 | 25 |

Table 2: Antimicrobial activity data of compounds.

in the complex [15]. The Co(II) complex has magnetic moment 3.23 B.M. also suggest an octahedral geometry. Ni(II) complex exhibits two electronic spectral bands at $\epsilon \sim 30 \text{ L mol}^{-1} \text{ cm}^{-1}$ and $\epsilon \sim 87 \text{ L mol}^{-1} \text{ cm}^{-1}$ which can be assigned to ${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ and ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ transitions in an octahedral field [5]. The transition due to ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ was completely obscured by the intense intra ligand transition band [12]. The spectral parameters of the Ni(II) complex are as follows [14]: $Dq = 1036.27 \text{ cm}^{-1}$, $B_1 = 740 \text{ cm}^{-1}$, $\beta = 0.719$ and $\beta_0 = 28.1\%$. The reduction of Racah parameter from the free ion value 1030 cm^{-1} and β_0 value of 28.1% confirms the presence of considerable covalence in the complex [14]. The Ni(II) complex has magnetic moment 2.19 B.M. also suggest an octahedral geometry. The Cu(II) complex exhibit broad band centered at $\epsilon \sim 95 \text{ L mol}^{-1} \text{ cm}^{-1}$ mainly due to ${}^2E_g \rightarrow {}^2T_{2g}$ transition suggesting the distorted octahedral geometry [13]. The observed magnetic moment value for Cu(II) complex is 2.25 B.M. suggestive of distorted octahedral nature for the complex [14]. Zn(II) complex does not demonstrate any characteristic d-d transitions and besides found to be diamagnetic in nature [12].

The perusal of antimicrobial activities of the compounds (Table 2) reveals that the complexes possess greater bactericidal and fungicidal activities against all the microbes in comparison to ligand which is due to their higher lipophilicity. This modified antimicrobial behavior of the complexes may be accounted for on the basis of Chelating Theory and Overtones Concept [15,16]. Among all the compounds Co(II) complex which showed highest antimicrobial activity against both test bacteria and antifungal activity against *Aspergillus niger* and greater than standard drugs, could be considered a promising drug against these microbes.

Conclusion

In this paper a new Schiff's base ligand, obtained by the coordination of ethylenediamine with 1-phenyl-2-(pyridin-2-yl)ethane-1,2-dione, has been used in the preparation of divalent transition metals, which are Ni(II), Cu(II), Co(II) and Zn(II) complexes. All the new products were characterized by using spectroscopic (UV-visible, FT-IR and AAS), molecular weight, elemental analysis, molar conductance and magnetic susceptibility measurements. FT-IR studies reveal the coordination of azomethine nitrogen and coordinating oxygen atoms to the metal ions. Magnetic measurements data in conjugation with electronic spectrum data revealed tetrahedral stereochemical of geometry of divalent metal complexes. Molar conductance values showed each complex were non-electrolytic nature. Elemental and metal analysis results are consistent to the molar formulae of the complexes. Antimicrobial studies conducted on two bacteria and two fungi revealed higher antimicrobial activities by complexes than the Schiff's base ligand against all the microbes used. That means Schiff's base ligand showed lowest activity than complexes of the metals.

Based on the current reports Schiff's bases and their complexes

are getting enhanced importance in their applications in treatment of varied transmissions including HIV and in other areas like in making light emitting diodes, water purification etc. I therefore, propose and recommend with confidence that the present Schiff's base ligand and other Schiff's bases could be synthesized to prepare complexes with transition metals of 3d, 4d and 5d series and products should be characterized for their structures and explored for their applications in different fields of interests.

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