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Synthesis, characterization and antimicrobial activity of some transition metal complexes of schiff base derived from o-phenylenediamine and 5-nitrosalicylaldehyde

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ABSTRACT

Iron, cobalt, nickel and copper complexes of a Schiff base derived from o-phenylenediamine and 5-nitrosalicylaldehyde were synthesized and characterized using elemental analyses, molar conductance measurements, infrared and electronic absorption spectroscopy. Elemental analysis data suggest the stoichiometry to be 1:1 [M:L] ratio formation in all complexes. Comparison of the IR spectra of the Schiff base and the metal complexes indicate that the Schiff base functions as a tetradentate ligand coordinated to the metal via the N_2O_2 chromophore. The electronic spectra data support octahedral geometry for iron(III) and cobalt(II) complexes and square planar geometry for nickel(II) and copper(II) complexes. The antimicrobial activity of the Schiff base and the metal complexes against some clinically important bacteria, namely *Staphylococcus aureus* (ATCC 25923), *Escherichia coli* (ATCC 25922), *Pseudomonas aeruginosa* (ATCC2384), and *Salmonella typhi* (ATCC14028) show that the activity was dependent on the geometry of metal complex and nature of coordinated groups to metal ion.

Keywords: o-phenylenediamine, Schiff base, metal complex, antimicrobial activity,

INTRODUCTION

Schiff bases have been subject of intense interest as a result of their synthetic accessibility and rich coordination chemistry. These compounds and their metal complexes have been reported to exhibit a wide spectrum of biological properties [1-3]. In particular, symmetrical Schiff bases derived from aromatic 1,2-diamines such as o-phenylenediamine have been shown to be useful models in understanding of biological systems such as irregular binding of peptides [4].

Earlier reports indicate that metal chelation improves biological activity of some bioactive organic compounds [5-6]. This prompted our interest in the effect of substituents and metal coordination on biological activity of metal complexes. Antimicrobial activity is a property of both organic and inorganic substances and the exploitation of such activity is of considerable importance in the development of antisepsics, sanitizers, germicides, bactericides and disinfectants [7]. In continuation of our study on the effect of metal ions on biological properties of o-phenylenediamine Schiff bases we herein report the antimicrobial activity and electronic absorption properties of cobalt, copper, iron and nickel complexes of symmetric Schiff base derived from o-phenylenediamine, and 5-nitrosalicylaldehyde

MATERIALS AND METHODS

Chemicals and solvents were of reagent or analytical grade and used without further purification.

o-phenylenediamine, 5-nitrosalicylaldehyde, copper(II) chloride, cobalt(II) chloride and nickel(II) chloride were purchased from Aldrich Sigma company and used as supplied.

Elemental analysis data were obtained on a Perkin Elmer model 2400 series II CHNS/O analyzer. Infrared (IR) spectra of the compounds were recorded as KBr discs on a Perkin-Elmer Spectrum RX1 spectrophotometer in the range 400 to 4000 cm^{-1} . ^1H NMR spectrum of the ligand was recorded in DMSO- d_6 solution on a Bruker Avance III 400 MHz spectrometer with chemical shifts reported in ppm relative to TMS as internal standard. The electronic absorption spectra of all the complexes were recorded in dimethylsulphoxide (DMSO) on a PGT80/T80⁺ UV-VIS spectrophotometer in 1cm quartz cell at room temperature immediately after preparing the solution. Conductivity measurements were obtained using N,N'-dimethylformamide (DMF) as solvent. Melting points were determined using a Gallenkamp melting-point apparatus and are uncorrected.

Synthesis of Schiff Bases (L)

To a hot stirred solution of *o*-phenylenediamine (1.08 g, 10 mmol.) in absolute ethanol (50 ml) was added a solution of 5-nitrosalicylaldehyde (3.44 g, 20 mmol.) in absolute ethanol (50 ml). This mixture was heated under reflux at 50 $^{\circ}\text{C}$ for 2 h, allowed to cool to room temperature and the yellow solid product formed was collected by filtration. The crude product was re-crystallized from ethanol.

Yield 3.99g (87.4%); M.P >230 $^{\circ}\text{C}$; IR (Nujol, cm^{-1}), 3692, 1619, 1373. UV (DMSO, nm) 265, 332; Anal calcd for $\text{C}_{20}\text{H}_{14}\text{N}_4\text{O}_6$, C: 59.12, H: 3.47, N: 13.79 found, C: 58.79, H: 3.48, N: 13.55.

General Synthesis of Metal Complexes

To a solution of the metal chloride (2 mmol.) in hot absolute ethanol (20 ml) was added a solution of **L** (2 mmol.) in hot absolute ethanol (40 ml). The solution was stirred and refluxed at 60 $^{\circ}\text{C}$ for 3 h. The precipitate formed was collected by filtration, washed with cold absolute ethanol and allowed to dry in a desiccator over silica gel.

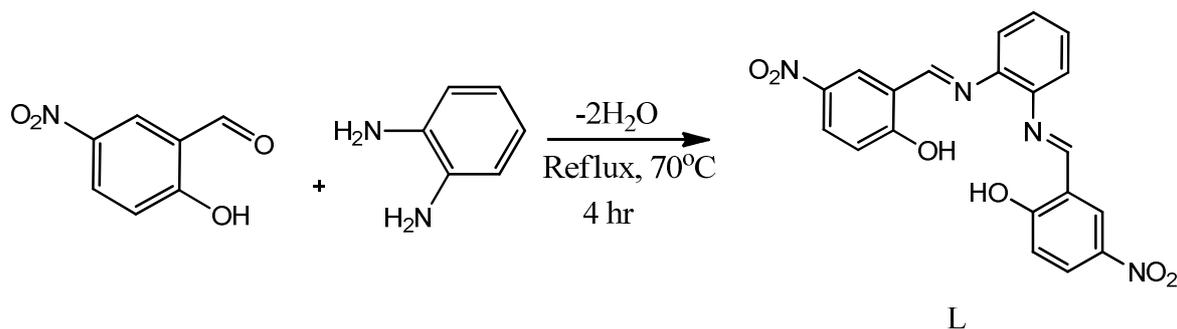
Antimicrobial study

The in-vitro antimicrobial activity of the investigated compounds were tested against standard strains of *Staphylococcus aureus* (ATCC25923), *Escherichia coli* (ATCC 25922), *Pseudomonas aeruginosa* (ATCC2384) and *Salmonella typhi* (ATCC 14028) using the Agar-ditch method [8]. The compounds were dissolved in dimethylformamide (DMF) to obtain a final concentration of 5 mg/ml. The bacterial strain was inoculated in 25 ml of Mac Conkey agar and incubated for 24 h at 37 $^{\circ}\text{C}$ in order to activate the bacterial strain. A solution of the activated bacterial strain was prepared in normal saline; the turbidity was adjusted using 0.5 McFarland standards. Molten Mueller-Hinton agar was poured over sterile 90 mm Petri dishes and 1ml of the activated strain was inoculated into the media when it reached a temperature of 40-45 $^{\circ}\text{C}$. The medium was allowed to solidify. A well was made in the plates with the help of a cork-borer (0.85 cm) which was then filled with the test sample solutions. Controls were run for each bacteria and the solvent. The plates were incubated at 37 $^{\circ}\text{C}$ for 24 h and the zones of inhibition formed by these compounds were measured at the end of the incubation period.

RESULTS AND DISCUSSION

Synthesis

The Schiff base ligand, **L** was isolated in good yield as a yellow solid from the reaction of *o*-phenyldiamine and 5-nitrosalicylaldehyde in a 1:2 stoichiometric ratio as illustrated in Scheme 1. Treatment of the ligand **L**, with Cu(II), Ni(II), Co(II) and Fe(III) chlorides, yielded complexes with empirical formula corresponding to metal : ligand ratio of 1:1. Analytical and physical data are presented in table 1. The metal complexes are soluble in common organic solvents such as DMF and DMSO. The low molar conductance values of the complexes in the range 4.42-9.65 $\mu\text{S}/\text{cm}$ indicate that all complexes behave as non-electrolytes [9].



Scheme1: Synthesis of Schiff base L

Table1. Physical and Analytical Data of Ligand (L) and Metal Complexes

| Empirical Formular | compd | m.w | Yield (%) | M.P °C | Colour | Microanalysis, calcd(found) | | | cond μS/cm |
|--|--------|-----|-----------|--------|-------------|-----------------------------|----------------|------------------|------------|
| | | | | | | %C | %H | %N | |
| C ₂₀ H ₁₄ N ₄ O ₆ | L1 | 406 | 87.0 | >230 | yellow | 59.12 (58.79) | 3.47 (3.48) | 13.79 (13.55) | |
| C ₂₀ H ₁₈ N ₄ O ₉ Co. | CoL1 | 522 | 80.9 | >300 | brown | 46.44 (45.86) | 3.51 (3.20) | 10.83 (11.10) | 7.42 |
| C ₂₀ H ₁₄ N ₄ O ₇ Ni. | NiL1 | 481 | 87.1 | >300 | orange | 49.94 (49.30) | 2.93 (2.95) | 11.65 (12.06) | 8.69 |
| C ₂₀ H ₁₄ N ₄ O ₇ FeCl | FeL1Cl | 516 | 86.0 | >300 | black | 46.77 (46.56) | 2.75 (2.71) | 10.91 (11.06) | 4.42 |
| C ₂₀ H ₂₂ N ₄ O ₁₁ Cu. | CuL1 | 461 | 73.1 | >300 | Dark yellow | 43.05 (43.01) | 3.97 (3.41) | 10.04 (12.46) | 8.13 |

Information from the IR spectra of the compounds was used to elucidate the bonding modes of the ligands to the metal ions. Important infrared spectra bands of the ligand and the metal complexes are listed in table 2. The absorption bands in the ligand at 1619 cm⁻¹ and 1350 cm⁻¹ attributed to the imine (C=N) and phenolic oxygen (C—O) groups were shifted to lower frequencies in all complexes. This indicates participation of the azomethine nitrogen and phenolic oxygen groups in metal ligand coordination. Further evidence of coordination of the Schiff base with the metals ion is revealed by the appearance of new bands at (740-749 cm⁻¹) and (406-566 cm⁻¹) assigned to the metal nitrogen (M—N) and metal-oxygen (M—O) vibration in all complexes. Thus the Schiff base functions as a tetradentate ligand coordinated *via* the azomethine nitrogen atom and the phenolic oxygen. The broad band at 3436 - 3269 cm⁻¹ in the metal complexes indicates the presence of coordinated water molecules

Table 2. Important IR and UV-vis Bands in Schiff base and Metal Complexes

| Compd | v(OH) | v(H ₂ O) | v(C=N) | v(C-O) | v(M-N) | v(M-O) | λ max (nm) |
|-------|-------|---------------------|--------|--------|-------------|-------------|---------------|
| L | 3692 | - | 1619 | 1350 | - | - | 265,332 |
| FeLCl | | 3367 | 1602 | 1312 | 549, 506 | 530, 406 | 330, 373, 444 |
| CoL | | 3436 | 1610 | 1328 | 740 | 538 | 316,381,462 |
| NiL | | 3367 | 1607 | 1322 | 744 | 544 | 405, 478 |
| CuL | | 3439 | 1612 | 1331 | 743 | 517 | 311, 403 |

Electronic Absorption Spectra

The electronic spectra of the ligand and metal complexes were recorded in DMSO in the range 600-220 nm and results are summarized in Table 2. The spectral data of the Schiff base shows two bands at 265 nm and 332nm due to $\pi-\pi^*$ and $n-\pi^*$ transitions [10]. The spectra of all metal complexes exhibit bands above 400 nm in addition to the $n-\pi^*$ transition in the ligand. In absence of X-ray diffraction studies, the electronic spectra can be used in determination of the structure of metal complexes as the number and position of spectral bands provide good insight to the geometry of a metal complex. In the present study, both Ni(II) and Cu(II) complexes are proposed to be in square planar environments. The band at 403 nm in the electronic spectrum of the Cu(II) complex is indicative of a ${}^2B_{1g} \rightarrow {}^2A_{1g}$ which is in conformity to a square planar geometry [11].

The appearance of a band at 478 nm in the Ni(II) complex as a result of $^1A_{1g} \rightarrow ^1B_{1g}$ transition favors a square planar geometry for Ni(II) complex. The intense absorption band at 462 nm assignable to $^4T_{1g}(F) \rightarrow ^4T_{1g}(P)$ in a high spin Co(II) complex [12] and charge-transfer band at 444 nm in the Fe(III) complexes suggests octahedral geometries for the two complexes [13]. Comparison of these results with the earlier studied complexes of 5-bromosalicylaldehyde [14] revealed that change in substituent from bromo to nitro group in the compounds studied did not affect the coordination geometry of the metal complexes.

Antimicrobial Activity

The antimicrobial activity of the investigated compounds against the microorganisms *E. coli*, *S. typhi*, *S. aureus* and *P. aeruginosa* was evaluated at a concentration of 5 mg mL⁻¹ using the agar ditch method [8]. The diameter of inhibition zones (mm) and the results are presented in table 3.

The compounds exhibited varying measure of activity against the microorganisms tested but none was active against *P. aeruginosa*.

Table 3: Antimicrobial activity of Schiff base ligand, L and their metal complexes (5mg/mL)

| Compound | Diameter of inhibition zone of bacteria (mm) | | | |
|----------|--|-----------------|----------------------|---------------|
| | <i>S.typhi</i> | <i>S.aureus</i> | <i>P. aeruginosa</i> | <i>E.coli</i> |
| L | 12 | 12 | - | 16 |
| FeL | 5 | - | - | 10 |
| CoL | 12 | 16 | - | 8 |
| NiL | 8 | 10 | - | 8 |
| CuL | 10 | 10 | - | 11 |
| DMF | - | - | - | - |

Control (DMF): - = No activity (there was no zone of inhibition)

The ligand was more active than the metal complexes against all bacterial strains with the activity recorded for the complexes varying with metal ion present. The activity of the complexes appears to be dependent on the geometry of the metal complex. The square planar complexes of Ni(II) and Cu(II) exhibited lower activity for all bacterial strains tested. The copper complex was moderately active for all bacteria except *P. aeruginosa*. The octahedral cobalt complex was highly active against the gram positive bacteria *S. typhi* and *S. aureus*. The poor activity of the iron complex may be due to the presence of coordinated halide ion. The halide ion being a π donor ligand increases the electron density on the metal ion. This contrary to the Overton concept [15] reduces lipophilicity of the complex thereby decreasing biological activity.

CONCLUSION

The synthesis of Cu(II), Co(II) Ni(II) and Fe(II) complexes of a Schiff base ligand, obtained from the reaction of *o*-phenylenediamine and 5-nitrosalicylaldehyde is described. The Schiff base acts as a tetradentate ligand coordinating to the metal ion through its azomethine *N* and phenolic *O* atoms. The electronic spectra indicate square planar geometries for Cu(II) and Ni(II) complexes with the Co(II) and Fe(II) complexes present in octahedral environments. The antimicrobial results showed that antimicrobial activity of the metal complexes depended both on the chelate geometry and groups coordinated to the metal.

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