Synthesis and Characterization of Schiff Base Complexes of Cu(II), Co(II) and Cd(II) Derived from Ethylenediamine and Benzaldehyde Derivatives

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Authors’ contributions

This work was carried out in collaboration among all authors. Author MRHA designed the study and performed the analysis. Author MSI performed the experiments and wrote the first draft of the manuscript. Authors MAF and MAA performed the analysis and edited the manuscript. All authors read and approved the final manuscript.

Article Information

DOI: 10.9734/AJACR/2020/v6i130150
Editor(s):
(1) Dr. Angélica Machi Lazarin, State University of Maringá, Brazil.
Reviewers:
(1) V. Gomathi, Seethalakshmi Ramaswami College (Affiliated to Bharathidasan University), India.
(2) Pravin N. Chavan, University of Mumbai, India.
Complete Peer review History: http://www.sdiarticle4.com/review-history/58162

Received 10 April 2020
Accepted 15 June 2020
Published 26 June 2020

Original Research Article

ABSTRACT

Metal complexes of Cu(II), Co(II) and Cd(II) have been synthesized using two new Schiff base ligands, N,N'-bis(4-chlorobenzylidene)ethane-1,2-diamine (L¹) and N,N'-bis(3-nitrobenzylidene)ethane-1,2-diamine (L²). The Schiff bases were prepared from the condensation reaction of ethylenediamine with benzaldehyde derivatives (4-chlorobenzaldehyde and 3-nitrobenzaldehyde). The complexes have been characterized by elemental analysis, conductivity measurements, UV-visible, FT-IR and magnetic susceptibility measurements. The magnetic susceptibility measurements and UV-visible spectral data revealed that the geometry of Cu(II) and Co(II) complexes are square planar, whereas the geometry of Cd(II) complex is tetrahedral. The molar conductance data showed that the complexes are non-electrolytic in nature. The complexes were screened for antibacterial activities against four human pathogenic bacteria viz. Escherichia coli, Shigella boydii, Bacillus cereus and Staphylococcus aureus. The results indicate that Cd(II) complex of ligand (L²) has higher antibacterial activity compared to the free ligands, but less than the standard drug, kanamycin. This suggests that the metal ion plays an important role in the antibacterial activities of complexes.

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Keywords: Schiff base; metal complexes; biological activity; magnetic moment; chelating ligands.

1. INTRODUCTION

Schiff bases derived from primary amines and carbonyl compounds are excellent chelating agents that coordinate to metal ions via azomethine nitrogen (≥C=N-) [1-5]. The azomethine group present in Schiff base ligands and its metal complexes has been reported due to their several biological applications including antibacterial, antifungal, antitumor, and antiuretic activities [6-10]. Moreover, Schiff base metal complexes are being used as biological models in understanding the structure of biomolecules and biological process. Instead, Schiff base metal complexes are also being explored as catalysts for organic reactions such as hydrogenation of olefins and carbonyl compounds, oxidation of organic compounds, complexing ability toward some toxic elements [11-15]. Schiff base metal complexes are used as growth inhibiting agents for most of microorganisms [5]. It has been reported that chelating ligands containing N and S as donor atoms show broad biological activity [16]. In a study of Prakash et al., (2010), Zn(II) and Cd(II) complexes derived from 4-nitrobenzaldehyde and acetophenone with ethylenediamine have been screened against E. coli and S. aureus bacteria. The activity data show that Zn(II) complexes have more bioactivity than the free ligands [1]. The Schiff base metal complexes are growing fast because of the wide variety of possible structures of the ligands derived from large number of carbonyl compounds and amines. In this work, Cu(II), Co(II) and Cd(II) metal complexes of symmetrical Schiff base ligands derived from ethylenediamine and benzaldehyde derivatives (4-chlorobenzaldehyde and 3-nitrobenzaldehyde) have been synthesized to explore their antimicrobial activity.

2. MATERIALS AND METHODS

2.1 Materials

All chemicals and solvents used in this study were of reagent grade. Melting points were obtained with an electro thermal melting point apparatus model o.AZ6512. IR spectra were recorded on a Jasco-8000 Fourier Transform Infrared Spectrophotometer from 400-4000 cm⁻¹ using KBr disc. The electronic spectra of the complexes in solution phase (0.0001 molar) were recorded in the region 200-800 nm on a Thermo-electron Nicolet evolution 300 UV-Vis spectrophotometer. The magnetic susceptibilities were measured on powdered samples using the Gouy Method. The conductance measurements were made at room temperature and 10⁻⁷M DMSO solution using a digital conductivity meter (CG 857 No. 71798 SCHOTT-GERATE Gumbo, Germany).

2.2 Synthesis of N,N'-bis(4-chlorobenzylidene)ethane-1,2-diamine Schiff Base Ligand (L¹)

4-chlorobenzaldehyde (40 mmol, 5.6228 g) was dissolved in ethanol (20 mL) in a clean round bottomed flask and ethylenediamine (20 mmol, 1.34 mL) was added drop wise to the solution with continuous stirring. The solution was refluxed for about four hours. Then it was allowed to stand for another half an hour. A white product was formed after cooling. The product was then filtered off, washed with ethanol and dried in vacuum desiccators over anhydrous CaCl₂ (Fig. 1a). The purity of the ligand was checked by TLC.

2.3 Synthesis of N,N'-bis(3-nitrobenzylidene)ethane-1,2-diamine Schiff Base Ligand (L²)

3-nitrobenzaldehyde (40 mmol, 6.052 g) was dissolved in ethanol (20 mL) in a clean round bottomed flask and ethylenediamine (20 mmol, 1.34 mL) was added drop wise to the solution with continuous stirring. The solution was refluxed for about four hours. Then it was allowed to stand for another half an hour. A white product was formed after cooling. The product was then filtered off, washed with ethanol and dried in vacuum desiccators over anhydrous CaCl₂ (Fig. 1b). The purity of the ligand was checked by TLC.

2.4 General Methods for the Synthesis of Metal Complexes

5 mmol of each hydrated salt [Cu(NO₃)₂·3H₂O], [Co(NO₃)₂·6H₂O], CdCl₂·H₂O dissolved in ethanol (10mL) was added slowly to ethanolic solution (20 mL) of Schiff bases (L¹ and L²) (10 mmol), respectively. The mixture was refluxed for 2 hours. Then the resulting solution was concentrated to half its volume and allowed to cool for another 1 hour. The complexes were separated out during cooling which were filtered off, washed several times with hot ethanol and finally dried in vacuum desiccators over anhydrous CaCl₂.
Fig. 1. Synthetic scheme of Schiff base ligands (a) \( L_1 \) and (b) \( L_2 \)

Fig. 2. Synthetic scheme of complexes using ligands (a) \( L_1 \) and (b) \( L_2 \)
2.5 Antibacterial Activity

Antibacterial activity of the ligands and complexes were measured against four pathogenic bacteria. Two of them were gram positive (Bacillus cereus, Staphylococcus aureus) and the other two were gram negative (Escherichia coli, Shigella boydii). The antibacterial activity of the ligands and complexes were determined by the standard disc diffusion method. The bacteria were grown in nutrient agar medium. The compounds to be tested were dissolved in DMSO. Then the plates were incubated at 37°C for 16 hours. After incubation, the diameter of zone of inhibition was measured in mm. The results were compared with the standard drug, kanamycine.

3. RESULTS AND DISCUSSION

The bidentate Schiff base ligands (L¹ and L²) have been synthesized by the condensation of ethylenediamine with two benzaldehyde derivatives, 4-chlorobenzaldehyde and 3-nitrobenzaldehyde, respectively as shown in Figs. (1a and b). The ligands were used to form the complexes (3-7) upon reaction with corresponding metal salts as shown in Figs. (2a and b). The elemental analyses (Table 1) of the ligands and complexes were consistent with the proposed formula. The molar conductance values of the complexes dissolved in 10⁻³ M DMSO solution were found in the range of 4-12 Ω⁻¹cm²mol⁻¹ indicating the non electrolytic nature of the complexes [1].

The infrared spectra of Schiff base ligands (L¹ and L²) showed a very strong absorption band in the region 1645-1646 cm⁻¹ (Table 2 and Figs. 3, 4), which is assigned for the azomethine ν(>C=N-) group [1-3]. The absorption band indicates that condensation has been taken place between the –NH₂ moiety of ethylenediamine and >C=O moiety of benzaldehyde derivatives. In the complexes, these absorption bands were shifted to lower frequency (1582-1620 cm⁻¹) which indicates that coordination of Schiff base to the metal centre has been occurred through the nitrogen atom of the azomethine group (Figs. 5-9). The coordination of the Schiff base ligands to the metal centre through the azomethine nitrogen atom reduces the electron density around the azomethine moiety which might be a reason of observed lower absorption frequency [1-5]. The formation of complexes has also been confirmed by the appearance of bands in the region of 475-545 cm⁻¹ due to ν(M-N) stretching [1,17]. The ligands and complexes showed broad band at (3400-3500) cm⁻¹ which might be attributed to stretching vibration ν(O-H) of hydrated water molecule [18].

The electronic spectral data and magnetic properties of the complexes are used in determining the structure of the complexes. The UV-visible absorption spectra of the ligands and metal complexes were recorded after dissolving them in DMSO at room temperature and shown in the Figures (Figs. 10-15). The electronic spectra of the ligands exhibited high intense absorption peaks at 274 and 288 nm which have been assigned to the π→π* and n→π* transitions, respectively of the azomethine group. The absorption spectra of the complexes shifted to longer wave lengths which also suggested that the chelation of the azomethine group to the metal centre has been accompanied through the azomethine nitrogen atom [19-21]. The electronic spectra of Cu(II) complexes (I and III) showed a broad band at 520-600 nm region which is assigned to d-d transition (²E₁g → ³T₁g), characteristics of square planar Cu(II) system. The magnetic moment of the Cu(II) complexes (I and III) has been found 1.92 B.M and 1.98 B.M. which further suggested a square planar geometry of d⁹ system of Cu(II). The Cd(II) complexes (II and V) did not show any absorption band in the visible region due to completely filled d¹⁰ electronic configuration of Cd²⁺ ion. The complexes exhibited band below 400 nm assigned to intra ligand charge transfer (ILCT) transition. The complexes are diamagnetic in nature due to completely filled d¹⁰ configuration of Cd²⁺ ion. The analytical, spectral and diamagnetic nature of the complexes are consistent with the proposed formula and suggested the tetrahedral geometry of Cd(II). The UV-visible absorption band of Co(II) complex (IV) exhibited absorption bands in the region 260-280 nm and 450 nm which might be attributed to the intra ligand charge transfer (ILCT) and ²B₁g → ³A₂g (P) transitions, respectively [1,5]. The magnetic moment of the complex is 2.75 B.M. at room temperature corresponding to one unpaired electron. Therefore, the electronic spectrum date and the magnetic susceptibility result suggested the square planar geometry of the Co(II) complex.
Table 1. Analytical data, molar conductance and magnetic moments of the compounds

| Compounds (Empirical formula) | Colors    | % yield | Melting point (°C) | Found (Cal)% | Ω⁻¹ (ohm⁻¹ cm² mol⁻¹) | ηeff (B.M.) |
|-------------------------------|-----------|---------|--------------------|--------------|-----------------------|-------------|
| L'(C₁₆H₁₄N₂Cl₂)              | White     | 92      | 205                | 63.48 (62.97)| 5.13 (4.19)           | 8.92 (9.18) | 0.0          |
| L²(C₁₆H₁₄N₂O₄)               | Off white | 90      | 132                | 57.35 (58.46)| 4.86 (5.10)           | 16.78 (17.14)| 0.0          |
| I(C₁₆H₁₄N₂Cl₂)₂Cu            | Green     | 85      | 225                | 58.91 (57.03)| 5.29 (4.19)           | 7.81 (8.31) | 10.17 (9.42) | 12           |
| II(C₁₆H₁₄N₂Cl₂)₂Cd           | White     | 72      | >300               | 54.49 (53.14)| 4.22 (3.90)           | 7.88 (7.75) | 16.20 (15.55)| 10           |
| III(C₁₆H₁₄N₂O₄)₂Cu           | Deep violet| 82     | 252                | 54.15 (53.67)| 3.99 (3.94)           | 16.10 (15.65)| 8.56 (8.87) | 9            |
| IV(C₁₆H₁₄N₂O₄)₂Co            | Coral     | 85      | 221                | 55.66 (54.08)| 4.21 (3.97)           | 16.45 (15.76)| 8.95 (8.16) | 4            |
| V(C₁₆H₁₄N₂O₄)₂Cd            | White     | 80      | 255                | 51.54 (50.24)| 3.87 (3.69)           | 15.05 (14.64)| 15.32 (14.70)| 7            |
### Table 2. IR (cm\(^{-1}\)) and UV-visible (nm) data of the compounds

| Compounds (Empirical formula) | \(\nu(C=N)\) | \(\nu(O-H)\) | \(\nu(M-N)\) | UV-visible, \(\lambda_{\text{max}}\) in nm |
|-------------------------------|-------------|-------------|-------------|-------------------------------------|
| \(L^1\) (C\(_{16}\)H\(_{14}\)N\(_2\)Cl\(_2\)) | 1645.34     | 3434.68     | -           | 274, 288                           |
| \(L^2\) (C\(_{16}\)H\(_{14}\)N\(_4\)O\(_4\)) | 1646.61     | 3435.19     | -           | 261                                |
| II[Cu(C\(_{16}\)H\(_{14}\)N\(_2\)Cl\(_2\))\(_2\)] | 1582.47     | 3306.32     | 524.38      | 260, 550                           |
| II[Cd(C\(_{16}\)H\(_{14}\)N\(_2\)Cl\(_2\))\(_2\)] | 1595.18     | 3467.79     | 616.97      | 271, 341                           |
| III[(C\(_{16}\)H\(_{14}\)N\(_4\)O\(_4\))\(_2\)Cu] | 1582.64     | 3309.20     | 524.53      | 259, 556                           |
| IV[(C\(_{16}\)H\(_{14}\)N\(_4\)O\(_4\))\(_2\)Co] | 1601.99     | 3400.61     | 596.56      | 260, 450                           |
| V[(C\(_{16}\)H\(_{14}\)N\(_4\)O\(_4\))\(_2\)Cd] | 1638.16     | 3435.27     | 544.11      | 258, 320                           |

**Fig. 3.** IR spectrum of the Schiff base Ligand, \(L^1\)

**Fig. 4.** IR spectrum of the Schiff base Ligand, \(L^2\)
**Fig. 5.** IR spectrum of the complex Cu-L$^1$

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**Fig. 6.** IR spectrum of the complex Cd-L$^1$
Fig. 7. IR spectrum of the complex Cu-L²

Fig. 8. IR spectrum of the complex Co-L²

Fig. 9. IR spectrum of the complex Cd-L²
Fig. 10. UV-visible spectra of the ligand $L^1$

Fig. 11. UV-visible spectra of the complex Cu-$L^1$

Fig. 12. UV-visible spectra of the complex Cd-$L^1$

Fig. 13. UV-visible spectra of the complex Cu-$L^2$

Fig. 14. UV-visible spectra of the complex Co-$L^2$

Fig. 15. UV-visible spectra of the complex Cd-$L^2$
Table 3. Antibacterial activity data of the ligands and its complexes

| Compounds Name/Standard | Compounds No. | Zone of inhibition (mm) against bacteria |
|-------------------------|---------------|----------------------------------------|
|                         |               | Bacillus cereus, (gram positive)       |
|                         |               | Staphylococcus aureus (gram positive)  |
|                         |               | Escherichia coli, (gram negative)      |
|                         |               | Shigella boydii (gram negative)        |
| Ligands                 | L1            | 0                                      |
|                         | L2            | 14                                     |
| Complexes               | I [Cu(C16H14N2Cl2)2] | 11                                     |
|                         | II [Cd(C16H14N2Cl2)2] | 12                                     |
|                         | III [(C16H14N4O4)2Cu] | 15                                     |
|                         | IV [(C16H14N4O4)2Co] | 0                                      |
|                         | V [(C16H14N4O4)2Cd] | 0                                      |
| Kanamycine              | Drug          | 35                                     |

Kanamycine Drug 35 35 30 30
The antibacterial activity of the ligands and its complexes were assessed against four pathogenic bacteria using the standard disc diffusion method. The microorganisms were grown in nutrient agar medium. The compounds to be tested were dissolved in DMSO. The diameter of zone of inhibition was measured in mm (Fig. 16). A blank DMSO containing sample showed no inhibition. The results are shown in Table 3. The results were compared with a standard drug, kanamycine. The bacterial screening results revealed that the complex II demonstrated maximum activity against both the gram negative bacteria, *Escherichia coli* and *Shigella boydii*, but less than the standard drug, whereas the ligand L\(^1\) showed moderately activity against both gram positive bacteria, *Staphylococcus aureus* and gram negative bacteria, *Shigella boydii*. Instead, the ligand L\(^2\) did not show any activity against gram negative bacteria, *Escherichia coli* and *Shigella boydii*. All other complexes except IV and V showed almost similar activity against both the gram positive and gram negative bacteria. Complexes IV and V did not show any activity against the gram positive bacteria. The variation in activities of the metal complexes against the bacterial strains depends on the different protein structure of the bacterial cell membrane and the polarity of the metal ions in the complexes. It has been reported that the polarity of metal ions reduces upon complexation because of the partial sharing of its positive charge with the donor groups within the chelate ring [21-23]. Therefore, the metal ion of the complexes might posses enhanced liphophilic nature which subsequently favors its diffusion.
through the lipid membrane of the microorganism resulting in higher activity. Moreover, nature of the metal ions, solubility, dipole moment and conductivity of complexes varies the antibacterial activity of the complexes.

4. CONCLUSIONS

Metal complexes of Cu(II), Co(II) and Cd(II) have been synthesized using the Schiff base ligands N,N'-bis(4-chlorobenzylidene)ethane-1,2-diamine (L₁) and N,N'-bis(3-nitrobenzylidene)ethane-1,2-diamine (L₂) derived from the condensation reaction of ethylenediamine with 4-chlorobenzaldehyde and 3-nitrobenzaldehyde, respectively. The elemental analysis, IR, UV-visible data suggested that the complexes were formed in 2:1 ligand to metal molar ratio. The conductivity measurements data revealed that the complexes are non-electrolytic in nature. The UV-visible and magnetic measurements data suggested the square planar geometry for Cu(II) and Co(II) complexes, whereas tetrahedral geometry for Cd(II) complexes. Cd(II) complexes derived from the ligand N,N'-bis(4-chlorobenzylidene)ethane-1,2-diamine (L₁) showed enhanced antibacterial activity against the gram negative bacteria: Escherichia coli and Shigella boydii compared to the free ligands.

ACKNOWLEDGEMENTS

The authors express their thanks to the Faculty of Science, Rajshahi University for providing financial support through the research grant and the Department of Chemistry, Rajshahi University for providing laboratory facilities. The authors also wish to express their gratitude to the Department of Pharmacy, Rajshahi University for providing laboratory facilities during the antibacterial activity test.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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