Synthesis Characterisation and anti-microbial properties of two Salicylaldimine Schiff base complexes of transition metals

Anaja Omanakuttan\textsuperscript{1}, G Priyanka \textsuperscript{1}, R Divya Mohan \textsuperscript{1,a)}

\textsuperscript{1}Department of Chemistry, Amrita School of Arts and Sciences, Amrita Vishwa Vidyapeetham, Amritapuri-690525, India.

\textsuperscript{a)}E-mail: divyamohanr@hotmail.com

Abstract. Schiff bases and their metal complexes are widely used in the area of pharmacology owing to their anti-microbial properties. In this article, we detail the synthesis of two metal complexes, viz. Cu(II) and Zn(II) complexes of a salicylaldimine Schiff base formed from ortho phenylene diamine (o-phdn) and salicylaldehyde. The complexes 1 [Cu(sal-o-phdn)] and 2 [Zn(sal-o-phdn)] are characterized by spectroscopic techniques like Fourier Transform Infrared spectroscopy (FT IR) and UV-Visible spectroscopic studies. The biological activity of the two complexes along with the Schiff base resistant to two gram positive and two gram negative bacteria is measured by Disc diffusion method. The complexes are found to be good candidates against certain microorganisms.

1. Introduction
Schiff base ligands and their complexes have attained much emphasis in the area of bioinorganic chemistry owing to their versatile applications in various fields including industrial processes and in biological, and analytical systems as effective antimicrobial agents\cite{1}-\cite{4} These are generated by the condensation between aldehydes/ketones with primary amines and are also called imine or azomethine. Many of them are reported as effective candidates in homogenous and heterogeneous catalysis as well due to their high thermal stability\cite{5}. The importance of Schiff bases lies in the fact that they act as chelating ligands and complex with transition metal ions producing biologically important complexes having applications as antifungal, antimicrobial, antiviral and antitumour agents\cite{6}. Many of these Schiff base complexes can act as model compounds in various biological reactions.

The coordination geometry of transition metals such as copper and zinc bivalent ions has encountered significant attention because of their applications as anti-microbial and anti-tumor agents. Ligands generated from salicylaldehyde and phenylene diamines are reported as effective multi dentate ligands which form four coordinated metal complexes with various transition metals\cite{7}-\cite{9}. They are able to perform tetra coordinated complexes with metals like Cu(II), Zn(II), Pt(II) etc. In the current article, we detail the synthesis and biological applications of two four coordinated copper (II) and zinc (II) complexes of bis orthophenylene diamine salicylaldehyde Schiff base. The complexes and the Schiff base are characterized by spectroscopic techniques like FT-IR and UV-Visible spectrophotometers and are well in agreement with the reported structures\cite{10}-\cite{11}. The complexes are further studied for their anti-microbial activity averse to the bacteria Klebsiella pneumonia, Salmonella typhi, Staphylococcus aureus and Bacillus subtilis. Results indicated that the complexes show moderate activity compared to the free ligand.
2. Experimental

2.1. Materials and Methods
Salicylaldehyde, ortho-phenylene diamine, copper nitrate and zinc nitrate are purchased from Merck. The Schiff base ligand bis(orthophenylenediamine) salicylaldehyde is prepared by employing known procedure[10] (Figure 1). The untaintedness of the ligand is detected by thin layer chromatography. FT-IR spectra of the Schiff base ligand and the complexes were recorded in solid phase as KBr discs on a Perkin Elmer IR spectrophotometer. UV-Visible spectra was jotted down on a Perkin Elmer UV-Visible spectrophotometer using dimethyl sulfoxide as the reference solvent. Anti-bacterial activity of the Schiff base and the complexes was measured by Disc diffusion method against various bacteria at CEPCI laboratories, Kollam, Kerala, India.

2.2. Preparation of metal complexes
About 0.1mmol of metal salt solution in DMF (N, N-dimethyl formamide) is slowly added to the Schiff base ligand taken in DMF, stirred well using a magnetic stirrer, warmed the solution in water bath for 3-4 hours. The precipitate floated is washed well with water and dried. Solubility of the complex is noted in many of solvents and is found to be soluble in dimethyl sulfoxide and dichloromethane. The complex is also partially being dissolved in methanol, ethanol and dimethyl formamide.

Figure 1. Formation of Schiff base complex of o-phenylene dimmine and salicylaldehyde (sal-o-phdn)

3. Results and Discussion

3.1. UV-Visible spectroscopic data
The electronic spectra of sal-o-phdn and the metal complexes are shown in Figure 2. The ligand depicts one strong band in the region 350nm which is present in the metal complexes as well. In addition, the complexes also exhibit one additional peak in the region 260nm. This may be due to the change in electron density due to complex formation. Moderate shift in $\lambda_{max}$ and $\varepsilon_{max}$ value of complexes can be understood as a result of change in electron distribution while complexing with metal ions.

Figure 2. UV-Visible spectra of Schiff base and the metal complexes

3.2. FT-IR spectroscopic data
The infrared spectra of sal-o-phdn manifest two strong bands around 1612 and 1585cm$^{-1}$ which may be assigned to (C=C) and (C=N) bond vibration ,a slight shift in wave numbers can be ascribable to the
change in the electron density upon complexation. The spectra of Schiff bases possess two intense bands in the region 3433-3054 cm⁻¹, because of hydrogen bonding interaction. Spectra of complexes 1 and 2 exhibit a wide band in the region 3435 cm⁻¹, for H₂O molecules this shows that Cu(II) and Zn(II) are coordinated with oxygen atoms. The assignments of various peaks for the ligand and the complexes are as listed in Table 1.

![FT-IR spectra of the Schiff base and the complexes 1 and 2.](image)

**Figure 3.** FT-IR spectra of the Schiff base and the complexes 1 and 2.

| Sal-o-phenH₂ | 1 (Zn) | 2 (Cu) | Assignments               |
|--------------|--------|--------|----------------------------|
| 3433.17      | 3435.43| 3435.90| O-H(H₂O)                   |
| 3054.20      |        |        | C-H (Aromatic)             |
| 2716.83      |        |        | C-H (Aliphatic)            |
| 1951.81      |        |        | C=C                         |
| 1612.31      | 1616.56| 1609.94|                            |
|              | 1586.37| 1581.01| C=N                         |

**Table 1.** FT-IR spectroscopic details of Schiff base and the complexes 1 and 2
3.3. Antimicrobial activity

The ligand and their metal complexes were subjected to biological activity resistant to two gram positive bacteria- Bacillus Subtilis and Staphylococcus Aureus and two gram negative bacteria- Salmonella Typhimurium and Klebsiella Pneumoniae. The samples were dissolved in DMSO and the analysis was performed by Disc diffusion method in agar medium. Out-turn denoted that complexes are more microbial toxic towards the gram positive bacteria Staphylococcus Aureus and show moderate microbial activity as indicated in Table 2. Lipophilicity plays the key role in controlling antimicrobial activity. The complexes increase the permeability of the lipophilic bacterial membrane by interacting with it. Hence, the complex can easily pierce into the membranes thereby inhibiting its further growth. However, it was also noted that the moderate activity of the Schiff base ligand towards the gram negative bacteria-Klebsiella Pneumoniae, is lost upon complexing with the Copper(II) and Zinc(II) metal ions.

Table 2. Antibacterial activity of the ligand and the complexes 1 and 2

| Compound     | S. Aureus | K. Pneumoniae | B. Subtilis | S. Typhimurium |
|--------------|-----------|---------------|-------------|----------------|
| Schiff base  | 0         | 8             | 0           | 0              |
| 1            | 5         | 0             | 0           | 0              |
| 2            | 8         | 0             | 0           | 0              |
Figure 4. Antibacterial activity of the ligand and its complexes. Zone of inhibition of the complexes against 1. Salmonella Typhimurium, 2. Klebsiella Pneumoniae, 3. Bacillus Subtilis, 4. Staphylococcus Aureus.

4. Conclusion

In conclusion, we have synthesised an azomethine Schiff base from salicylaldehyde and 1,2-phenylene diamine and is complexed with the bivalent transition metals Copper and Zn. The complexes are characterised using FT IR and UV Visible spectroscopic studies. The metal complexes were assessed for anti-bacterial activity against various bacteria. The results showed that both the metal complexes have more microbial toxicity towards the gram positive bacteria Staphylococcus Aureus than the Schiff base ligand.

5. Reference

[1] K. R. Joshi, A. J. Rojivadiya, and J. H. Pandya, “Synthesis and Spectroscopic and Antimicrobial Studies of Schiff Base Metal Complexes Derived from 2-Hydroxy-3-methoxy-5-nitrobenzaldehyde,” Int. J. Inorg. Chem. Vol., vol. 2014, 2014.

[2] H. Luo et al., “Synthesis and Evaluation of in Vitro Antibacterial and Antitumor Activities of Novel N,N-Disubstituted Schiff Bases,” Biochem. Res. Int., vol. 2017, 2017.

[3] A. S. Gaballa, M. S. Asker, A. S. Barakat, and S. M. Teleb, “Synthesis, characterization and biological activity of some platinum(II) complexes with Schiff bases derived from salicylaldehyde, 2-furaldehyde and phenylenediamine,” Spectrochim. Acta - Part A Mol. Biomol. Spectrosc., vol. 67, no. 1, pp. 114–121, 2007.

[4] C. D. Sheela, C. Anitha, P. Tharmaraj, and D. Kodimunthri, “Synthesis, spectral characterization, and antimicrobial studies of metal complexes of the schiff base derived from [4-amino-N-guanylbenzene sulfonamide] and salicylaldehyde,” J. Coord. Chem., vol. 63, no. 5, pp. 884–893, 2010.
[5] K. C. Gupta and A. K. Sutar, “Catalytic activities of Schiff base transition metal complexes,”
Coord. Chem. Rev., vol. 252, no. 12–14, pp. 1420–1450, 2008.

[6] N. Zhang et al., “Syntheses, crystal structures and anticancer activities of three novel transition metal complexes with Schiff base derived from 2-acetylpyridine and l-tryptophan,” Inorg.
Chem. Commun., vol. 22, pp. 68–72, 2012.

[7] S. Bhagat, N. Sharma, and T. S. Chundawat, “Synthesis of some salicylaldehyde-based schiff bases in aqueous media,” J. Chem., vol. 2013, 2013.

[8] L. J. Althaher, “Synthesis and Characterization of Mn Synthesis and Characterization of Metal Complexes of Cu(II), Ni(II), Zn(II), Co(II), Mn(II) and Cd(II) with Tetradeutate Schiff Bases,”
Raf. J. Sci., vol. 24, no. 4, pp. 25–33, 2013.

[9] A. M. Abu-Dief and I. M. A. Mohamed, “A review on versatile applications of transition metal complexes incorporating Schiff bases,” Beni-Suef Univ. J. Basic Appl. Sci., vol. 4, no. 2, pp.
119–133, 2015.

[10] M. N. Uddin and M. A. Salam, “Bis(salicylaldehyde)phenylenediamine—a noble reagent for the trace determination of metal ions in environment,” Research, vol. 1, no. May 2014, 2014.

[11] Antony F, Marinovich, R. Shane O’Mahony, Joyce M Waters and T. Neil M. Waters 1999
Croat. Chem. Acta. 72 p 685-703.