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# STRUCTURAL ANALYSIS WITH ANTIMICROBIAL ACTIVITY OF THE U(VI) AND Zr(IV) METAL COMPLEXES WITH SCHIFF BASE 2-[(2-AMINO-ETHYLIMINO)-METHYL]-PHENOL AND HETEROCYCLIC AMINES

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**Abstract.** A series of Schiff base complexes of U(VI) and Zr(IV) containing heterocyclic amines has been prepared. The complexes were isolated from the reaction in solid forms and characterized by IR, $^1$H NMR, UV- Vis., and some physical measurements. The observed values confirmed that the complexes have octahedral geometry with diamagnetic nature. The complexes have been found to have moderate to strong antimicrobial, antifungal and cytotoxic activity.

***Keywords:*** *U(VI) and Zr(IV) metal complex, Heterocyclic amine, Antimicrobial activity, Schiff base.*

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## 1. Introduction

Peroxo complexes have received considerable importance in recent years due to their application as oxidation catalyst (Nasrin & Islam, 2007) and biochemical relevance (Singh *et al.*, 2012). They are widely used in oxidation of thioanisole, methyl benzene, tertiary amines, alkenes, alcohols, bromine (Cho *et al.*, 2011; Cenini *et al.*, 1985; Westland & Tarafder, 1981; Mugesh *et al.*, 2001). These are also known to act as herbicides, insecticides and acaricides (Sabastiyan & Venkappayya, 1992). Peroxo metal complexes also have broad application in biological processes (Sabastiyan & Venkappayya, 1992; Kudrat-E-Zahan *et al.*, 2015; Kudrat-E-Zahan & Islam, 2015; Shiraj-U-Ddaula *et al.*, 2014; Islam, 2014). Their metallurgical and biological activities have been widely studied (Nasrin, 2015a; Nasrin, 2015b). Therefore, Studies on the well defined heteroligand peroxo-metal complexes therefore is an important prerequisite for a heuristic approach in this field of chemistry. Peroxo transitional metals complexes are sources of active oxygen atoms and many of these complexes can be used as efficient stoichiometric as well as catalytic oxidants for organic and inorganic substrate (Bonchio *et al.*, 1999; Bonchio *et al.*, 1997).

In this study we report the synthesis, characterization and antimicrobial activity of U(VI) and Zr(IV) metal complexes with Schiff base 2-[(2-Amino-ethylimino)-methyl]-phenol and heterocyclic amines.

## 2. Experimental

### *2.1 Reagent and chemicals*

All the reagents used were of analar or chemically pure grade. Solvents were purified and dried according to standard procedures.

### *2.2 Physical measurements*

The melting or decomposition temperatures of all the prepared metal complexes were observed in an electro thermal melting point apparatus model No.AZ6512. The SHERWOOD SCIENTIFIC Magnetic Susceptibility Balance was used for the present investigation. Infrared spectra as KBr disc were recorded in a Shimadzu FTIR-8400 (Japan) infrared spectrophotometer, from 4000-400 $cm^{-1}$. The absorbance of the complexes in methanol were recorded in the region 200-800 nm on a thermoelectron Nicolet evolution 300 UV-Visible Spectrophotometer.

## 3. Preparation

### *3.1 General method of preparation of Schiff base 2-[(2-amino-ethylimino)-methyl]-phenol (SB)*

The Schiff base was prepared by the condensation of salicyldehyde with ethylenediamine. Salicylaldehyde (1.7g, 0.014 mol) in absolute ethanol (20 mL) was added to an ethanolic solution of ethylenediamine (0.8414 ml, 0.014 mol). The mixture was heated to reduce the volume to 25 mL, and then it was cooled in an ice bath. The colored product was isolated and washed with hot ethanol and dried in a vacuum desiccator over anhydrous $CaCl_2$.

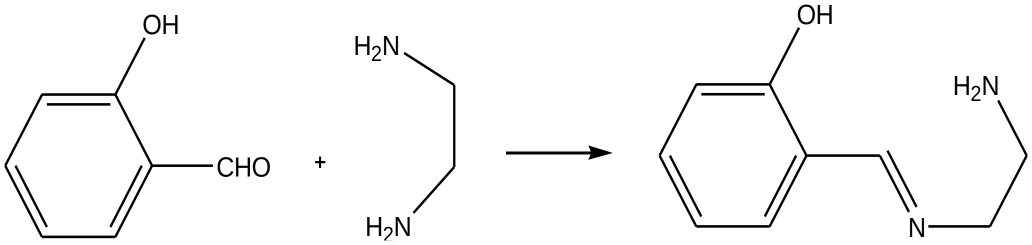

**Figure 1.** Structure of Schiff Base 2-[(2-Amino-ethylimino)-methyl]-phenol (SB)

### *3.2. General method for the preparation of Schiff Bases (SB) complexes*

General formula: [M(SB)L]Cl; Where, M= U(VI) and Zr(IV). L=Heterocyclic amines/ Quinoline, Iso-quinoline, 2-picoline, and 4-picoline.

0.002 mol of metal salt, 0.002 mol of SB and 0.004 mol of KOH were separately dissolved in ethanol and the solutions were mixed and heated on a water bath for half an hour. Then an ethanolic solution of 0.002 mol of “L” was added to the mixed solution. The resultant solution was heated under reflux on a water bath for 2hours and then cooled. The coloured precipitate so formed was filtered, washed with hot ethanol and dried in a vacuum desiccator over anhydrous $CaCl_2$.

## 4. Results and discussion

### *4.1. Physical properties of the complexes:*

The physical properties of the complexes are listed in Table 1. The reported metal complexes are coloured, non-hygroscopic and electrolyte in nature. The magnetic susceptibility measurement showed that all the complexes are diamagnetic in nature. All the complexes are stable at room temperature.

**Table 1.** Physical properties of the complexes

| **Complex** | **Colours** | **Yields (%)** | **Decomp. temp. ± 5 °C** | **Molar Conductace $Ohm^{-1}Cm^{2}mol^{-1}$** | **Magnetic moment $\mu_{eff}$ (B.M.)** |
|---|---|---|---|---|---|
| [U(SB) Q]Cl | Yellow | 70 | 210 | 82.50 | 0.434 |
| [U(SB)IQ]Cl | Greenish Yellow | 65 | 198 | 73.90 | 0.414 |
| [U(SB) (Py)]Cl | Yellow | 68 | 165 | 78.30 | 0.644 |
| [U(SB)(2-Pic)]Cl | Orange Red | 70 | 185 | 75.40 | 0.525 |
| [Zr(SB)Q]Cl | Cream | 67 | 140 | 74.40 | 0.29 |
| [Zr(SB)IQ]Cl | White | 65 | 122 | 77.20 | 0.432 |
| [Zr(SB) (Py)]Cl | Brown | 65 | 135 | 79.80 | Dia |
| [Zr(SB)(2-Pic)]Cl | Cream | 66 | 132 | 84.30 | Dia |

Where, SB: $C_9H_{11}NO_2$, Q: Quinoline, IQ: Iso-quinoline, 2-Pic: 2-Picoline and Py: Pyridine.

### *4.2. Electronic spectra of the complexes*

The electronic spectra data (Table 2) of the complexes showed bands between 230-370 nm regions due to the charge transfers band only

**Table 2.** Electronic spectral data of the complexes

| **Complexes** | **$\lambda_{max}$(nm)** | |
|---|---|---|
| Ligand/SB | 300 | 340 |
| [U(SB)Q]Cl | 298 | 345 |
| [U(SB)IQ]Cl | 255 | 345 |
| [U(SB) (Py)]Cl | 260 | 290 |
| [U(SB)(2-Pic)]Cl | 280 | 325 |
| [Zr(SB)Q]Cl | 260 | 295 |
| [Zr(SB)IQ]Cl | 315 | 350 |
| [Zr(SB) (Py)]Cl | 310 | 360 |
| [Zr(SB)(2-Pic)]Cl | 320 | 370 |

Where, SB: $C_9H_{11}NO_2$, Q: Quinoline, IQ: Iso-quinoline, 2-Pic: 2-Picoline and Py: Pyridine

### *4.3. IR Studies of the complexes*

Infrared spectral data have been represented in Table 3. The complexes display ν(C=N) bands at (1638-1550) $cm^{-1}$ significantly lower than the values of the Schiff base ν(C=N) at 1650 $cm^{-1}$. These indicate the coordination of Schiff base through their ν(C=N) group. The U(VI) complexes display ν(M=O) modes in the region (936-825) $cm^{-1}$ [16]. Further, the presence of ν(M-O) and ν(M-N) modes at the region (836-725) and (501-459) $cm^{-1}$ respectively. The complexes display ν(N-H) modes in the region of ν(3468-3435) $cm^{-1}$.

**Table 3.** IR spectral data of the complexes

| Complexes | **ν(N-H) $cm^{-1}$** | **ν (C=N) $cm^{-1}$** | **ν (M=O) $cm^{-1}$** | **ν(M-O) $cm^{-1}$** | **ν(M-N) $cm^{-1}$** |
|---|---|---|---|---|---|
| Ligand/(SB) | 3450 | 1650 | - | - | - |
| [U(SB)Q]Cl | 3468 | 1579 | 882 | 725 | 501 |
| [U(SB) (Py)]Cl | 3459 | 1629 | 918 | 760 | 463 |
| [U(SB)(2-Pic)]Cl | 3435 | 1550 | 825 | 724 | 459 |
| [Zr(SB)Q]Cl | 3468 |  | - | 836 | 463 |
| [Zr(SB) (Py)]Cl | 3436 | 1638 | - | 825 | 457 |

Where, SB: $C_9H_{11}NO_2$, Q: Quinoline, 2-Pic: 2-Picoline and Py: Pyridine.

### *4.4. $^1$H NMR Studies of the complexes*

The NMR spectra of complexes can account all the protons of the ligand in complexes except phenolic proton which are lost during complex formation i,e. deprotonation of the ligand. This is the evidence of coordination via, phenolic oxygen of the ligand. A singlet in the range of 7-8 ppm. Due to azomethine proton of the ligand. Multiplet peaks in the range of 6-7 ppm are due to phenyl protons of salicyldehyde. The complexes show two separate peaks at 3.3 ppm (for $–CH_2$ proton) and 9.5ppm (for $–NH_2$ proton).

**Table 4.** $^1$H NMR spectral data of the complexes

| Complexes | Phenyl proton(ppm) | Azomethine Proton(ppm) | $-CH_2$ proton(ppm) | $-NH_2$ proton(ppm) |
|---|---|---|---|---|
| [U(SB)Q]Cl | 6.96 | 7.61 | 3.33 | 9.465 |
| [Zr(SB)Q]Cl | 6.78 | 7.84 | 3.59 | 9.75 |

Where, SB: $C_9H_{11}NO_2$, Q: Quinoline.

From the above information and data the probable structure of the U(VI) complex is given below in Fig. 2:

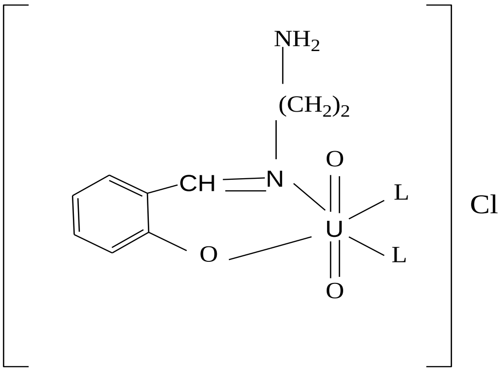

**Figure 2.** Proposed structure of U(VI) complexes. Where, L= Heterocyclic amines e,g, Quinoline, Isoquinoline and 2-Picoline

## 5. Antibacterial activity of the metal complexes

The susceptibility of microorganism to antimicrobial agents can be determined *in vitro* by a number of methods. The disc diffusion technique is widely acceptable for preliminary investigations of compounds, which are suspected to possess antimicrobial properties. Antimicrobial activities of the test samples are expressed by measuring the zone of inhibition observed around the area.

The present results revealed that the complexes are more microbial toxic than the free metal ions or ligands. The U(VI) and Zr(IV) metal Schiff bases complexes (Table 5) showed moderate activity against both Gram positive and Gram negative bacteria compared to standard Kanamycine.

**Table 5.** Antibacterial activity of the complexes and *Kanamycin*

| **Complexes** | **Zone of inhibition, diameter in mm** | | | |
|---|---|---|---|---|
| | **Gram Negative** | | **Gram Positive** | |
| | ***E. coli*** | ***Shigella dysenteriae*** | ***Agro bactrium*** | ***Bacillus subtilis*** |
| [Zr(SB)Q]Cl | 07 | 06 | 06 | 06 |
| [Zr(SB)Py]Cl | 08 | 08 | 08 | 06 |
| [U(SB)Q]Cl | 07 | 09 | 08 | 07 |
| [U(SB)Py]Cl | 07 | 08 | 06 | 08 |
| *Kanamycin -30* | 28 | 20 | 21 | 25 |

Where, SB: $C_9H_{11}NO_2$, Q: Quinoline, 2-Pic: 2-Picoline and Py: Pyridine.

## 6. Antifungal activity of the metal complexes

The antifungal activities of all the metal Complexes and standard fluconazole (F-50 μg/ml)) were determined at the concentration of 100 μg/ml disc against four pathogenic fungi. The results of the antifungal activity of the complexes are recorded in Table 6. From the zone of inhibition it is observed that all the complexes showed significant activity towards all the fungi used. The highest antifungal activity were shown in the complexes U(VI) and Zr(IV) against *Saccharromycess* (9 mm) and *Candida albicaus* (9 mm) respectively (Table 6).

**Table 6.** Antifungal activity of the complexes against *Saccharromycess*(SC), *Aspergillus niger* (AN), *Candida albicaus*(CA)

| **Complexes** | **Diameter of zone inhibition (mm) 200μg/disc** | | |
|---|---|---|---|
| | SC | AN | CA |
| [Zr(SB)Py]Cl | 6 | 7 | 9 |
| [U(SB)Q]Cl | 7 | 0 | 6 |
| [U(SB)2-Pic]Cl | 9 | 8 | 6 |

Where, SB: $C_9H_{11}NO_2$, Q: Quinoline, IQ: Iso-quinoline, 2-Pic: 2-Picoline and Py: Pyridine.

## 7. Cytotoxic activity of the metal complexes

Brine Shrimp lethality bioassay is a development in the bioassay for the bioactive compounds. Here, *in vivo* lethality in a simple zoological organism (brine shrimp nauplii) is used as a convenient monitor for screening and fractionation in the discovery of new bioactive products. In this bioassay, the mortality rate of brine shrimp was found to increase with the increase of concentration of the samples. The test complexes showed positive results in brine shrimp lethality bioassay. So these complexes are bioactive (Table 7).

**Table 7.** Brine shrimp lethality bioassay for test complexes

| **Complexes** | **24h Exposure** |
|---|---|
| | **$LC_{50}$ (µg/ mL)** |
| [Zr(SB)Q]Cl | 17.78 |
| [Zr(SB)Py]Cl | 39.80 |
| [U(SB)Q]Cl | 28.84 |
| [U(SB)Py]Cl | 28.84 |

Where, SB: $C_9H_{11}NO_2$, Q: Quinoline, and Py: Pyridine.

## 8. Conclusion

It is concluded that the physical and analytical data were in good agreement with the proposed emperical formulae of both the complexes. All the complexes are non-hygroscopic diamagnetic and electrolyte in nature. The complexes of U (VI) showed strong activity against both the gram positive and gram negative bacteria than the other complexes indicating the higher zone of inhibition. Results showed that the complex [Zr(SB)Q]Cl exhibits more toxic to brine shrimp compared to other complexes of Zr(IV) and U(VI) indicating the lower values of $LC_{50}$ for the exposure of 24h. Hence, this study will help the researchers to develop new antimicrobial agents.

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