

## Synthesis, Spectral Studies and Antimicrobial Activity of Schiff Bases Derived from 4,4'-Diaminodibenzyl with Substituted Salicylaldehydes and Metal Complexes with Mn(II), VO(II) and UO<sub>2</sub>(II)

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A series of polydentate Schiff bases have been prepared by the condensation of 4,4'-diaminodibenzyl with different aldehydes such as salicylaldehyde and substituted salicylaldehydes. The Schiff bases characterized by elemental analysis and spectral methods. The metal complexes of Mn(II), VO(II) and UO<sub>2</sub>(II) have been prepared by the reaction of Schiff bases. The analytical and spectral data support the octahedral structure for Mn(II) and UO<sub>2</sub>(II) and square pyramidal for VO(II) complexes. The antimicrobial activities of Schiff bases and their metal complexes have been studied by screening the compounds against micro organisms such as *E. coli*, *S. typhi*, *B. subtilis* and *S. aureus*.

**Key Words:** Schiff bases, 4,4'-Diaminodibenzyl, Oxovanadium, Dioxouranium, Manganese, Antimicrobial activity.

### INTRODUCTION

The Schiff bases have remarkable property of forming complexes. The Schiff bases and their metal complexes show a wide spectrum of applications such as biochemical<sup>1</sup>, analytical<sup>2</sup>, industrial<sup>3</sup> and antimicrobial<sup>4</sup> agents. The present paper describes the synthesis of Mn(II), VO(II) and UO<sub>2</sub>(II) complexes using Schiff bases derived by the condensation of 4,4'-diaminodibenzyl with salicylaldehyde, 5-bromo- and 5-chlorosalicylaldehyde. The compounds have been characterized by the elemental analysis, electrical conductivity, IR, NMR, Mass, Electronic spectral data, magnetic susceptibility measurements, thermal studies and XRD study. The antimicrobial activities of the compounds against some selected organisms have also been reported.

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## EXPERIMENTAL

All the chemicals used were of a AR grade. 4,4'-Diaminodibenzyl was obtained from M/s Fluka Chemicals, salicylaldehyde, 5-bromosalicylaldehyde and 5-chlorosalicylaldehyde, manganese acetate, vanadyl sulphate and uranyl nitrate were purchased from Aldrich.

IR spectra of Schiff bases and metal complexes were recorded on a Perkin Elmer FTIR spectrophotometer model 1600 using KBr. Electronic spectra of Schiff bases in  $\text{CHCl}_3$  and metal complexes in DMSO solution were recorded on a Perkin Elmer Lambda-35 UV/Visible spectrometer.  $^1\text{H}$  NMR spectra were recorded on Bruker-400 MHz NMR spectrometer in  $\text{CDCl}_3$ . The DI Mass spectra of Schiff bases were recorded on Shimadzu GC-MS instrument. The molar conductance of complexes at  $10^{-3}$  M solution in DMSO was measured on Elico Model CM-180 direct reading conductivity meter with dip-type conductivity cell. Magnetic susceptibilities were measured by Gouy balance using  $\text{Hg}[\text{Co}(\text{SCN})_4]$  as a calibrant. The thermal data of complexes were recorded on instrument model DSC Q 100. XRD study done on Powder X-ray diffractometer, Make and Model PAN alytical, Xpert PRO.

**Preparation of Schiff bases:** A solution of salicylaldehyde (24.42 g 0.2 mol) in 25 mL ethanol was added drop wise over 0.5 h to a stirred solution of 4,4'-diaminodibenzyl (21.23 g 0.1 mol) dissolved in 300 mL warm ethanol. The yellow suspension formed was stirred and refluxed on water bath for *ca.* 2-3 h. The product was filtered and washed successively with ethanol and recrystallized from xylene (yield 90 %). The Schiff bases of 5-bromosalicylaldehyde and 5-chlorosalicylaldehyde were isolated similarly.

**Preparation of complexes:** The Schiff base (0.01 mol) suspended in 100 mL methanol was added to sodium hydroxide (0.02 mol) solution in water. The suspension was heated on water bath and a reddish-brown solution was formed. The reaction mixture was cooled by  $5^\circ\text{C}$  temperature and metal salt (0.02 mol) in 25 mL methanol was added dropwise. The resulting mixture was refluxed under stirring for 4 h on water bath. The separated product was filtered and washed with methanol. All the complexes were dried in open air and kept in vacuum desiccator.

## RESULTS AND DISCUSSION

All the complexes are stable, crystalline, intense coloured and non-hygroscopic. They are insoluble in common organic solvent but soluble in excess DMSO. Metal content in the complexes was determined by standard literature methods<sup>5</sup> which is supported by AAS analysis. On the basis of analytical data (Table-1) the metal chelates were found to have 1:1 (metal: ligand) stoichiometry. The molecular weight of ligands are in good

agreement with the molecular ion peak in mass spectra. The molar conductance value of the complexes in DMSO at 10<sup>-3</sup> M concentration are low in the range of 0.11-0.26 ohm<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>, suggesting that the compounds are non electrolytes<sup>6</sup>. The decomposition temperature of the complexes determined in the laboratory are recorded in Table-1. These values are close to those observed in the thermal analysis and show the thermal stability of metal chelates.

TABLE-1  
PHYSICAL AND ANALYTICAL DATA OF SCHIFF BASES  
AND THEIR METAL COMPLEXES

| Compound/<br>(Colour)  | m.w. /<br>m.p. (°C) | Found (Calcd.) % |                |                |                  | $\mu_{\text{eff}}$ (BM) |
|--|---------------------|------------------|----------------|----------------|------------------|-------------------------|
|  |                     | C                | H              | N              | M                |                         |
| [H <sub>2</sub> -HSalPDADB]<br>(Pale yellow)                             | 420.51<br>(231)     | 79.50<br>(79.97) | 5.80<br>(5.75) | 6.71<br>(6.66) | -                | -                       |
| [H <sub>2</sub> -BrSalPDADB]<br>(Yellow)                                 | 578.30<br>(272)     | 58.31<br>(58.15) | 3.88<br>(3.83) | 4.70<br>(4.84) | -                | -                       |
| [H <sub>2</sub> -ClSalPDADB]<br>(Yellow)                                 | 489.40<br>(254)     | 68.91<br>(68.72) | 4.53<br>(4.53) | 5.65<br>(5.72) | -                | -                       |
| [Mn(HSalPDADB)(H <sub>2</sub> O) <sub>2</sub> ] <sub>2</sub><br>(Brown)  | 1018.92<br>(>300)   | 66.40<br>(66.01) | 5.47<br>(5.14) | 5.65<br>(5.49) | 10.70<br>(10.78) | 5.55                    |
| [Mn(BrSalPDADB)(H <sub>2</sub> O) <sub>2</sub> ] <sub>2</sub><br>(Brown) | 1335.03<br>(>300)   | 50.10<br>(50.38) | 3.28<br>(3.62) | 4.25<br>(4.19) | 8.32<br>(8.23)   | 5.70                    |
| [Mn(ClSalPDADB)(H <sub>2</sub> O) <sub>2</sub> ] <sub>2</sub><br>(Brown) | 1156.70<br>(299)    | 58.88<br>(58.15) | 4.25<br>(4.18) | 5.00<br>(4.86) | 9.76<br>(9.49)   | 5.50                    |
| [VO(HSalPDADB)] <sub>2</sub><br>(Green)                                  | 970.86<br>(>300)    | 69.30<br>(69.28) | 4.49<br>(4.57) | 5.71<br>(5.77) | 10.40<br>(10.49) | 1.68                    |
| [VO(BrSalPDADB)] <sub>2</sub><br>(Green)                                 | 1286.46<br>(292)    | 52.35<br>(52.28) | 3.20<br>(3.13) | 4.28<br>(4.35) | 8.11<br>(7.92)   | 1.62                    |
| [VO(ClSalPDADB)] <sub>2</sub><br>(Greenish)                              | 1108.64<br>(>300)   | 60.38<br>(60.67) | 3.71<br>(3.64) | 5.18<br>(5.05) | 9.22<br>(9.19)   | 1.72                    |
| [UO <sub>2</sub> (HSalPDADB)] <sub>2</sub><br>(Orange)                   | 1377.04<br>(>300)   | 48.71<br>(48.84) | 3.30<br>(3.22) | 4.10<br>(4.07) | 34.60<br>(34.57) | Dimag-<br>netic         |
| [UO <sub>2</sub> (BrSalPDADB)] <sub>2</sub><br>(Orange)                  | 1692.62<br>(>300)   | 39.90<br>(39.74) | 2.40<br>(2.38) | 3.38<br>(3.31) | 28.16<br>(28.12) | Dimag-<br>netic         |
| [UO <sub>2</sub> (ClSalPDADB)] <sub>2</sub><br>(Yellow Orange)           | 1514.82<br>(>300)   | 44.61<br>(44.40) | 2.56<br>(2.66) | 3.60<br>(3.70) | 31.33<br>(31.43) | Dimag-<br>netic         |

The physical and analytical data of all the three Schiff bases are given in Table-1. Mass spectral data is good agreement with the molecular weight of Schiff bases. The thermal stability of the reagents as reflected in their melting points, increases in the order:



The IR spectra of Schiff bases show the absorption of  $\text{-HC=N-}$  azomethine group at around  $1617\text{ cm}^{-1}$  consistent with the iminic absorption at  $1630\text{-}1610\text{ cm}^{-1}$  of the free salicylidenic Schiff bases<sup>7</sup>. The presence of a strong band in the range  $1280\text{-}1275\text{ cm}^{-1}$  region is typical of phenolic stretching band  $\nu(\text{C-O})$  and indicates the presence of an enol-iminic structure in the salicylidene<sup>8</sup> moiety. The medium intensity broad band at around  $2925\text{ cm}^{-1}$  shows the existence of intramolecular hydrogen bonding between the phenolic oxygen and azomethinic nitrogen  $\nu(\text{OH}) (\text{OH}\cdots\text{N})$ <sup>9</sup>. The IR spectra show that all the three ligands exist in the enol-iminic form (Fig. 1) which is further supported by  $^1\text{H NMR}$  studies. In the spectra of  $\text{H}_2\text{-HSalPDADB}$ ,  $\text{H}_2\text{-BrSalPDADB}$  and  $\text{H}_2\text{-ClSalPDADB}$  the azomethine proton ( $\text{-HC=N-}$ ) exhibit a chemical shift, respectively at 8.65, 8.54 and 8.52 ppm typical of the enolic form<sup>10</sup>. The sharp low-field signals for the two phenolic protons were found, respectively at 13.34, 13.30 and 13.20 ppm. This shows that the Schiff bases form intramolecular hydrogen bonds involving the phenolic proton and the azomethine nitrogen atom and show an enol-iminic structure<sup>11</sup>. The multiplet signal corresponding to aromatic protons occurs in the range 6.80-7.46 ppm while resonance signals due to methylene ( $\text{-CH}_2\text{-}$ ) protons occur in the range 3.02-3.10 ppm.

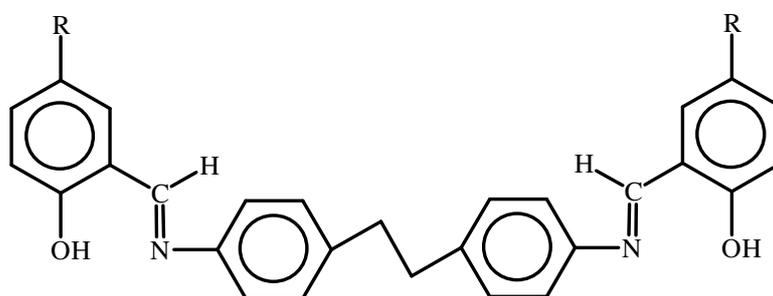


Fig. 1. Structure of Reagents:  $\text{N,N'}$ -bis-[5-R-salicylidene]-4,4'-diaminodibenzyl [ $\text{H}_2\text{-RSalPDADB}$  ( $\text{R} = \text{-H, -Br, -Cl, -}$ )]

The Schiff bases  $\text{H}_2\text{-HSalPDADB}$ ,  $\text{H}_2\text{-BrSalPDADB}$  and  $\text{H}_2\text{-ClSalPDADB}$  show a medium broad band in the range of  $2920\text{-}2893\text{ cm}^{-1}$  which may be assigned to the phenolic  $\nu(\text{OH})$  stretching vibrations<sup>9</sup>. This band disappears in spectra of complexes indicating the dissociation of phenolic hydrogen with bond formation between metal and oxygen<sup>12</sup>. This is further supported by the shift to higher frequency ( $60\text{-}70\text{ cm}^{-1}$ ) of  $\nu(\text{C-O})$  vibrations observed at around  $1270$  in free ligand to  $1350\text{ cm}^{-1}$  in metal complexes which is also confirmed by the appearance of a new, low intensity band in the region  $595\text{-}580\text{ cm}^{-1}$  in the spectra of complexes due to  $\nu(\text{M-O})$  vibrations<sup>13</sup>. A strong and sharp band at  $1618\text{-}1617\text{ cm}^{-1}$  in the

spectrum of the ligands due to  $\nu(\text{C}=\text{N})$  shows a shift to lower frequency in the spectra of all complexes which indicates the coordination of azomethine nitrogen to the metal ions. This is again supported by the appearance of a new low intensity band<sup>14</sup> in the region 498-460  $\text{cm}^{-1}$  in complexes are attributable to  $\nu(\text{M}-\text{N})$  vibrations. The spectra of oxovanadium(IV) complexes show new bands in the range 960-940  $\text{cm}^{-1}$  which are assigned<sup>15</sup> to  $\nu(\text{V}=\text{O})$  vibrations. In the dioxouranium(VI) complexes bands at around 970-960  $\text{cm}^{-1}$  are assigned to  $\nu(\text{O}=\text{U}=\text{O})$  modes<sup>15</sup>.

The magnetic moment values of the Mn(II) complexes are 5.55, 5.70 and 5.50 BM which are in the range required for six-coordinated spin free octahedral complexes<sup>16</sup> further supported by electronic spectral data. The magnetic moments obtained for the oxovanadium(IV) complexes are in the range 1.62-1.72 BM these values are in the vicinity of spin only values of VO(II) complexes reported<sup>17</sup> earlier. The UO<sub>2</sub>(II) complexes are diamagnetic in nature.

The Mn(II) complexes exhibits three bands in the range 16,000-21,000, 24,100-26,600 and 28600-29,000 corresponds to transition  ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{1g}(\text{G})$  ( $\nu_1$ ),  ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{1g}(\text{G})$  ( $\nu_2$ ) and  ${}^6\text{A}_{1g} \rightarrow {}^4\text{E}_g(\text{G})$  ( $\nu_3$ ), respectively. The electronic spectra of oxovanadium(IV) complexes exhibit three bands in the region 22100-13,200  $\text{cm}^{-1}$ . Several models have been proposed in the literature<sup>18,19</sup> for the interpretation of the electronic spectra of oxovanadium(IV) complexes. The electronic spectra of these complexes have identical features indicating similar geometries around vanadium. The isolated oxovanadium(IV) complexes show all the expected three bands in the region 13,200-13,700, 16,250-16,850 and 21,150-22,200  $\text{cm}^{-1}$ . Of these the first band reveals its identity as a broad band, where as second band occurs as a weak band and the third band appearing around 21,500  $\text{cm}^{-1}$  may be due to the charge transfer transition between  $d_z^2$  orbital of vanadium and  $2p_x$  or  $2p_y$  orbital of oxygen atom. The first and second bands are assigned to  ${}^2\text{B}_2 \rightarrow {}^2\text{E}$  and  ${}^2\text{B}_2 \rightarrow {}^2\text{B}_1$  transitions, respectively. On the basis of available data the complexes have been assigned the square pyramidal structures<sup>20</sup>. The electronic spectra of UO<sub>2</sub>(II) complexes do not show any characteristic  $d-d$  transitions except charge transfer bands. The UO<sub>2</sub>(II) complexes have eight coordination with octahedral geometry.

The decomposition of complexes of Mn(II), VO(II) and UO<sub>2</sub>(II) takes place at high temperature. The decomposition of complexes at high temperature indicates that they are thermally very stable.

**Antimicrobial activity:** The Schiff bases and their metal complexes were screened for antibacterial activities by ditch plate method<sup>21</sup>. The activity of the compounds was tested against *Escherichia coli*, *Salmonella typhi*, *Bacillus subtilis* and *Staphylococcus aureus*. The sterile nutrient agar used as a medium which was kept at 37°C for 24 h. The bacterial culture

used were 24 h old. The growth from the slants was suspended in sterile saline and used for testing against the compounds. The two different concentrations 3 and 5 mg of the compounds were used.

All the ligands are inactive but ligand prepared from chlorosalicylaldehyde is active against *Staphylococcus aureus* and their Mn(II), VO (II) and UO<sub>2</sub>(II) complexes were found inactive at both concentrations against different types of bacteria used, only oxovanadium complexes of H<sub>2</sub>-BrSalPDADB and H<sub>2</sub>-ClSalPDADB active against *Escherichia coli* and *Salmonella typhi*, respectively. (Table-2).

TABLE-2  
ANTIMICROBIAL ACTIVITY OF SCHIFF BASES AND  
METAL COMPLEXES

| Compound  | <i>E. coli</i> |      | <i>S. typhi</i> |      | <i>B. subtilis</i> |      | <i>S. aureus</i> |      |
|---|----------------|------|-----------------|------|--------------------|------|------------------|------|
|   | 3 mg           | 5 mg | 3 mg            | 5 mg | 3 mg               | 5 mg | 3 mg             | 5 mg |
| [H <sub>2</sub> -HSalPDADB]                                   | -              | -    | -               | -    | -                  | -    | -                | -    |
| [H <sub>2</sub> -BrSalPDADB]                                  | -              | -    | -               | -    | -                  | -    | -                | -    |
| [H <sub>2</sub> -ClSalPDADB]                                  | -              | -    | -               | -    | -                  | -    | +                | ++   |
| [Mn(HSalPDADB)(H <sub>2</sub> O) <sub>2</sub> ] <sub>2</sub>  | -              | -    | -               | -    | -                  | -    | -                | -    |
| [Mn(BrSalPDADB)(H <sub>2</sub> O) <sub>2</sub> ] <sub>2</sub> | -              | -    | -               | -    | -                  | -    | -                | -    |
| [Mn(ClSalPDADB)(H <sub>2</sub> O) <sub>2</sub> ] <sub>2</sub> | -              | -    | -               | -    | -                  | -    | -                | -    |
| [VO(HSalPDADB)] <sub>2</sub>                                  | -              | -    | -               | -    | -                  | -    | -                | -    |
| [VO(BrSalPDADB)] <sub>2</sub>                                 | +              | +    | -               | -    | -                  | -    | -                | -    |
| [VO(ClSalPDADB)] <sub>2</sub>                                 | -              | -    | +               | ++   | -                  | -    | -                | -    |
| [UO <sub>2</sub> (HSalPDADB)] <sub>2</sub>                    | -              | -    | -               | -    | -                  | -    | -                | -    |
| [UO <sub>2</sub> (BrSalPDADB)] <sub>2</sub>                   | -              | -    | -               | -    | -                  | -    | -                | -    |
| [UO <sub>2</sub> (ClSalPDADB)] <sub>2</sub>                   | -              | -    | -               | -    | -                  | -    | -                | -    |

- Not active, ++ Very active, + Moderately active

**XRD studies:** As an extension of this work further study on powder XRD for some representative Schiff base and their metal complexes indicates that these are crystalline and can be indexed to orthorhombic system.

### Conclusion

The spectral data show that the Schiff bases exist in enol-iminic form and behave as tetradentate ligands by bonding to the metal ion through the phenolic oxygen and azomethine nitrogen. The analytical data show the presence of one metal ion per ligand molecule and suggest a mononuclear structure for the complexes (Fig. 2). The magnetic moment values and electronic spectral data are in the favour of a octahedral geometry for Mn(II) and UO<sub>2</sub>(II) complexes and square pyramidal structure for VO(II) complexes. The microbial study of the present compounds shows only two VO(II) complexes are active against *Escherichia coli* and *Salmonella typhi*, all remaining complexes are not active against all the bacteria used.

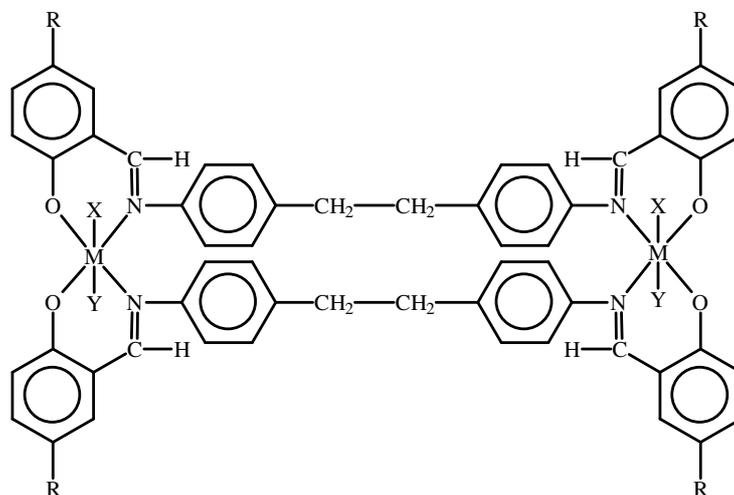


Fig. 2. Proposed structure for Mn(II), VO(II) and UO<sub>2</sub>(II) complexes  
 Mn(II) : X = H<sub>2</sub>O and Y = H<sub>2</sub>O; VO(II) : X = O and Y = Nil  
 UO<sub>2</sub>(II) : X = O and Y = O; (R = -H, -Br, -Cl)

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