

## Studies on Metal Complexes of Schiff Bases Derived from Sulphadiazine and Sulphadimidine with 5-Substituted Salicylaldehydes

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Oxovanadium(IV), iron(III), cobalt(II), nickel(II) and copper(II) complexes of schiff bases derived from sulphadiazine and sulphadimidine with 5-nitrosalicylaldehyde and 5-chlorosalicylaldehyde have been prepared and characterized by elemental analysis, IR, magnetic moment and electronic spectral data. The schiff bases and their metal complexes have also been subjected to fungicidal screening for studying their antifungal activity.

### INTRODUCTION

Schiff bases derived from sulphadiazine and salicylaldehyde have been found to be good fungicides<sup>1</sup>, bactericides<sup>2,3</sup> as well as chelating agents<sup>4,5</sup>. In the present work, we are reporting the isolation and characterization of VO(IV), Fe(III), Co(II), Ni(II) and Cu(II) complexes with schiff bases derived from sulphadiazine and sulphadimidine with 5-nitrosalicylaldehyde and 5-chlorosalicylaldehyde.

### EXPERIMENTAL

The compounds 5-nitrosalicylaldehyde and 5-chlorosalicylaldehyde were synthesized from salicylaldehyde (S.M.) by usual methods<sup>6</sup>. The schiff bases of sulphadiazine and sulphadimidine with 5-nitrosalicylaldehyde and 5-chlorosalicylaldehyde were prepared as earlier<sup>5</sup> and abbreviated as SDZNS, SDZCS, SDMNS and SDMCS respectively. Their metal complexes were prepared as earlier<sup>5</sup>.

### RESULT AND DISCUSSION

Analytical data revealed that VO(IV), Co(II), Ni(II) and Cu(II) have 1 : 2 (metal : ligand) stoichiometry while Fe(III) complexes have been found to have 1 : 3 (metal : ligand) stoichiometry.

The schiff bases show broad IR-absorption bands at *ca* 3420 which is obviously due to the intramolecular hydrogen bonding involving hydrogen of the phenolic group and nitrogen atom of imine group<sup>7,8</sup>. This band has not been observed in complexes indicating the replacement of phenolic hydrogen by metal ion and formation of M-O bond. The ligand also showed a strong absorption band at *ca* 1260 due to  $\nu(\text{C-O})$  which appeared in the complexes at *ca* 1305. This shift further supports the

formation of M-O bond<sup>9, 10</sup>. Another important band observed at *ca* 1645 in Schiff bases due to  $\nu\text{C}=\text{N}$  shifts at  $1625 \pm 5$  in metal complexes. This shows the formation of M-N band<sup>10</sup>. The spectra of oxovanadium(IV) complexes also showed a strong absorption band at *ca* 985 assignable to V=O band and suggesting a monomeric<sup>11</sup> structure for such complexes. Some new bands of medium and low intensity have also been observed in IR spectra of complexes at  $580 \pm 10$  and  $510 \pm 10$  assignable to  $\nu(\text{M}-\text{O})$  and  $\nu(\text{M}-\text{N})$  stretching vibration frequencies respectively. These bands may also be coupled with the ligand bands<sup>9</sup>. Besides these significant changes, the complexes also showed a number of bands of strong and medium intensity characteristic of  $\text{SO}_2\text{NHR}$  (*ca* 3080),  $-\text{SO}_2-\text{I}$  & II (*ca* 1340 & *ca* 1150) and heterocyclic ring (*ca* 1580) almost at the same frequency as in Schiff bases indicating lack of coordination through these groups.

The value of magnetic moment in the oxovanadium complexes have been found to be 1.83–1.88 B.M. indicated presence of one free electron in them. Their electronic spectra have been characterized by the presence of three spectral bands at  $12500\text{--}12900\text{ cm}^{-1}$ ,  $17600\text{--}18000\text{ cm}^{-1}$  and  $26300\text{--}26900\text{ cm}^{-1}$  corresponding to the transitions  ${}^2\text{B}_2 \rightarrow {}^2\text{E}$ ,  ${}^2\text{B}_2 \rightarrow {}^2\text{B}_1$  and  ${}^2\text{B}_2 \rightarrow {}^2\text{A}_1$  respectively<sup>12</sup>. The values of Dq, Ds and Dt were found to be  $1760\text{--}1800\text{ cm}^{-1}$ ,  $3000\text{--}3114\text{ cm}^{-1}$  and  $685.8\text{--}737.4\text{ cm}^{-1}$  respectively and are in good agreement with the reported values<sup>13, 14</sup> for VO(IV) complexes having  $\text{C}_{4v}$  symmetry. The value of tetragonal distortion<sup>15</sup> i.e.  $\frac{\text{DT}}{\text{DQ}}$  has also been calculated and found to be 0.248–0.260. Spin orbit coupling coefficient  $\lambda$  has also been calculated and its value lies in the range  $164.5\text{--}168.3\text{ cm}^{-1}$ . This value is in good agreement with the reported value ( $170\text{ cm}^{-1}$ ) for such complexes<sup>16, 17</sup>.

Iron(III) complexes showed magnetic moment value 5.89–5.93 B.M. characteristic of octahedral geometry<sup>18</sup>. Such complexes exhibited four spectral bands in their electronic spectra at  $13900\text{--}14100\text{ cm}^{-1}$  [ ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{1g}(\text{G})$ ],  $18800\text{--}19200\text{ cm}^{-1}$  [ ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{2g}(\text{G})$ ],  $24300\text{--}24700\text{ cm}^{-1}$  [ ${}^6\text{A}_{1g} \rightarrow {}^4\text{E}_g(\text{G})$ ] and  $27900\text{--}28300\text{ cm}^{-1}$  (charge transfer). The values of Dq, B' and  $\beta$  (covalency factor) have been found to be  $1390\text{--}1410\text{ cm}^{-1}$ ,  $1245\text{--}1281\text{ cm}^{-1}$  and 0.958–0.986 respectively. The values of Conden Shortley parameters ( $\text{F}^2$  &  $\text{F}^4$ ) and transition  $\pi \rightarrow \pi^*$  have been found to be 95.84–98.63 kK, 62.75–64.56 kK and  $38400\text{--}38900\text{ cm}^{-1}$  respectively. These values are in the vicinity of the standard value  $\text{F}^2 = 81\text{ kK}$ ,  $\text{F}^4 = 50.27\text{ kK}$  and  $\pi \rightarrow \pi^* 38280\text{ cm}^{-1}$ .

Cobalt(II) complexes were found to have  $\mu$  eff 4.51–4.54 B.M., a value characteristic of tetrahedral<sup>19</sup> geometry. Their electronic spectra exhibited only two spectral bands at  $7100\text{--}7400\text{ cm}^{-1}$  and  $15700\text{--}16600\text{ cm}^{-1}$  respectively assignable to transition  ${}^4\text{A}_2(\text{F}) \rightarrow {}^4\text{T}_1(\text{F})$  and  ${}^4\text{A}_2(\text{F}) \rightarrow {}^4\text{T}_1(\text{P})$  respectively. The values of  $10\text{Dqt}$ , B',  $\beta$  and  $-\lambda$  have been found to be  $3944\text{--}4111\text{ cm}^{-1}$ ,  $731.1\text{--}777.8\text{ cm}^{-1}$ , 0.752–0.801 and  $169.96\text{--}173.1\text{ cm}^{-1}$  respectively.

The nickel(II) complexes of Schiff bases prepared were found to be diamagnetic in character, a property characteristic of square planar stereochemistry. Three spectral bands were observed in their electronic spectra at 16500–17000  $\text{cm}^{-1}$  [ ${}^1A_{1g} \rightarrow {}^1A_{2g}$ ], 20300–21100  $\text{cm}^{-1}$  [ ${}^1A_{1g} \rightarrow {}^1E_g$ ] and 27500–28200  $\text{cm}^{-1}$  [ ${}^1A_{1g} \rightarrow {}^1B_{1g}$ ]. The values of parameters  $\Delta_1$ ,  $\Delta_2$ , and  $\Delta_3$  on calculation<sup>22</sup> were found to be 18950–19450  $\text{cm}^{-1}$ , 4850–5050  $\text{cm}^{-1}$  and 7450–7550  $\text{cm}^{-1}$  respectively.

As expected Cu(II) complexes showed magnetic moment 1.85–1.89 B.M. characteristic value for the presence of one free electron. They exhibited three well defined spectral bands at 13800–14200  $\text{cm}^{-1}$ , 20000–20200  $\text{cm}^{-1}$  and 25000–25300  $\text{cm}^{-1}$  corresponding to [ ${}^2B_{1g} \rightarrow {}^2A_{1g}$ ], [ ${}^2B_{1g} \rightarrow {}^2E_g$ ] and charge transfer transitions respectively. These values indicate obviously square planar geometry for Cu(II) complexes because tetrahedral complexes give a single broad band in the near IR region and no absorption between 10000–20000  $\text{cm}^{-1}$  while square planar complexes<sup>20, 21</sup> show absorption in the range 14000–18000  $\text{cm}^{-1}$ .

### Fungicidal Activity

The Schiff bases as well as their complexes of Fe(III), Co(II), Ni(II) and Cu(II) have been subjected to Growth Method<sup>22</sup> for studying their fungicidal activity against various fungi viz. *Alternaria alternata*, *Curvularia lunata* and *Fusarium oxysporum* at 100, 50 and 20 ppm concentrations using Czapeck's Dox agar medium. Percentage inhibition<sup>23</sup> was calculated using the formula:

$$\% \text{ Inhibition} = \frac{C - T}{C} \times 100$$

where

C = Diameter of fungus colony in control plates after 168 hrs

T = Diameter of fungus colony in treated plates after 168 hrs.

Fungitoxicity data reveals that complexes have comparatively lower % inhibition than corresponding Schiff bases. The fungitoxicity of complexes have been found in the order: Cu(II) > Ni(II) > Co(II) > Fe(III). However, the fungitoxicity showed a gradual increase with increase in concentration. Schiff bases derived from sulphadimidine were found to be more toxic than those derived from sulphadiazine. Similarly, chloro compounds showed more fungicidal activity than nitro compounds.

### ACKNOWLEDGEMENT

One of the authors (SG) is grateful to UGC, New Delhi for awarding Teacher Fellowship.

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[Received: 3 March 1989; Accepted: 27 October 1989]

AJC-106