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**Synthesis, characterization and potentiometric studies of a novel Schiff base and its metal complexes**

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**ABSTRACT:** Condensation of Ni(II) ion with a Schiff base, SB derived from salicylaldehyde and valine afforded a 1:1 complex Ni(SB).H<sub>2</sub>O. It was characterized by IR, UV-visible, mass spectra, magnetic moment and conductivity measurement data. The molar conductance reveals a non-electrolytic nature while the magnetic moment value indicates that the Ni(II) complex is paramagnetic. The electronic spectral data exhibit  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  transitions. The mass spectral data show the formation of 1:1 complex. A tetrahedral geometry has been proposed for the Ni(II) ion in the complex. The stability constants of the Schiff base complexes with divalent transition metal ions at variable temperature (25 and 30 °C) and at constant ionic strength ( $\mu = 0.1$  M) have been evaluated from potentiometric data. The stability of the complexes has been found to be inversely proportional to the temperature. The negative value of  $\Delta G^\circ$  and  $\Delta H^\circ$  can be corroborated from the spontaneous and exothermic nature of these reactions.

**Keywords:** Salicylaldehyde, valine, Schiff base complexes, Potentiometric studies

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## INTRODUCTION

“Privileged ligands” is the name coined for Schiff base ligands because of their ease of preparation. These compounds have attracted tremendous interest in the area of material and biological chemistry<sup>1,2</sup>. They find important catalytic applications in asymmetric epoxidation<sup>3</sup>, Lewis acid assisted organic transformations<sup>4</sup>, and solid phase extraction of metal ions<sup>5</sup>, and in the preparation of ion selective electrodes<sup>6</sup>. They have also been employed as antibacterial, anticancer and antifungal agents<sup>7,8</sup>. Schiff base complexes of copper derived from salicylaldehydeacetylhydrazone (H<sub>2</sub>sa) and salicylaldehydebenzoylhydrazone, [Cu(Hsb)Cl]H<sub>2</sub>O have been demonstrated to possess antitumor and radio-protective activity<sup>9</sup>. Some of the metal complexes have been found to be potent inhibitor of DNA synthesis and cell growth than the free Schiff bases<sup>10</sup>. Several transition metal complexes of Schiff bases derived from appropriate carboxylic acid ester and hydrazine hydrate have been synthesized and a QSAR investigation of cytotoxicity against a human adenocarcinoma cell line was carried out<sup>11</sup>. Copper(II) complexes have been found to be markedly more cytotoxic than the free ligands. Furthermore, Schiff bases are also employed as starting material in the synthesis of industrial and biological compounds such as  $\beta$ -lactones. Some of these are used as model molecules for biological oxygen carrier systems<sup>12</sup>. In case of macrocyclic Schiff base the cavity can provide limited space for specific metal ions allowing successful synthesis of homo and heterometallic complexes with varied stereochemistry<sup>13,14</sup>. This feature is employed for modeling active sites in biological systems. They can be used as oxygen conveyer, electron transfer agents and stereo specific catalysts for oxidation<sup>15</sup>.

The present study aims to synthesis and characterize a novel Schiff base derived from salicylaldehyde and valine and its Ni(II) complex. The stability constants of Schiff base metal complexes may eventually help to shed light on the inactivation of essential trace metals in biological systems. It has also been of interest to determine the protonation and stability constants of Schiff base metal complexes of Mn(II), Fe(II), Co(II), Ni(II) and Cu(II) ions. The logK,  $\Delta G^\circ$ ,  $\Delta H^\circ$  and  $\Delta S^\circ$  have been evaluated to gain information regarding the bonding and exploring the factors responsible for enhancement of stability in solution.

## CHEMICALS AND METHODS

All chemicals were obtained from BDH or Aldrich and Analar grade solvents were used. Ethanol was distilled prior to use. Elemental analysis (C, H and N) was carried out with Perkin-Elmer 2400 elemental analyzer. IR spectra (4000-400cm<sup>-1</sup>) were recorded with IFS-25DPUS/IR Bruker spectrometer as KBr disc. The Electronic spectra were recorded with Perkin-Elmer Lamda 4B spectrophotometer in CHCl<sub>3</sub>. The conductivity measurement was carried out on a CMD-650 digital conductivity meter in CHCl<sub>3</sub>. Magnetic susceptibility measurement was done with Sherwood Scientific Instrument (England) at room temperature. The mass spectra were run using Q-1000 EXGC-MS Shimadzu spectrometer at 70 eV using a direct insertion probe at temperature 90-110 °C.

### Preparation of solutions

All the stock solutions were prepared in double distilled water. Ionic strength was maintained at 0.1 M. Low concentrations of Schiff base (0.001 M) and transition metal halides (0.001 M) were used. The following mixtures were prepared and titrated against 0.2 M NaOH.

Solution A: 0.1N HCl (5 mL) + 1M NaCl (4.5 mL) + water

Solution B: 0.1N HCl (5 mL) + 1M NaCl (4.5 mL) + 0.001M SB (20 mL) + water

Solution C: 0.1N HCl (5 mL) + 1M NaCl (4.5 mL) + 0.001M SB (20 mL) + 0.001M MCl<sub>2</sub> (5 mL) + water.

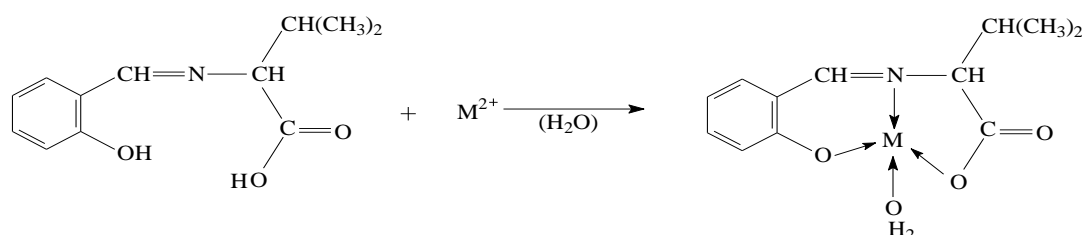
The total volume was kept at 50 mL in all the cases. The measurements were made at 25 and  $30 \pm 1$  °C. The measurements were carried out with Elico L1-120 pH meter fitted with combined glass electrode.

### Synthesis of Schiff base, SB

The Schiff base was prepared by the condensation of salicylaldehyde (0.01 mol, 1.22 g) with valine (0.01 mol, 1.17 g) in dry ethanol. The mixture was refluxed for two hours and left overnight to yield bright yellow crystals. It was washed and recrystallized with hot ethanol. The purity of crystals was checked by TLC, Yield 82%.

### Synthesis of Ni(II)-Schiff base complex, Ni(SB).H<sub>2</sub>O

A mixture of the Schiff base (0.01 mol, 2.21 g) and NiCl<sub>2</sub>.6H<sub>2</sub>O (0.01 mol, 2.37 g) in 50 ml ethanol was stirred followed by the addition of a few drops of ammonia and refluxed for three hours. The product thus obtained was washed twice with ethanol and dried *in vacuo*.



**Scheme- 2: Probable structure of the NiSB.H<sub>2</sub>O complex**

### Results and Discussion

The elemental analysis of Ni(SB).H<sub>2</sub>O corresponds to the formation of a 1:1 complex (Table.1). The molar conductivity of the complex measured in chloroform is far below the value for an electrolyte<sup>16</sup>.

**Table- 1. Some physicochemical properties of the Schiff base and its Ni(II) complex.**

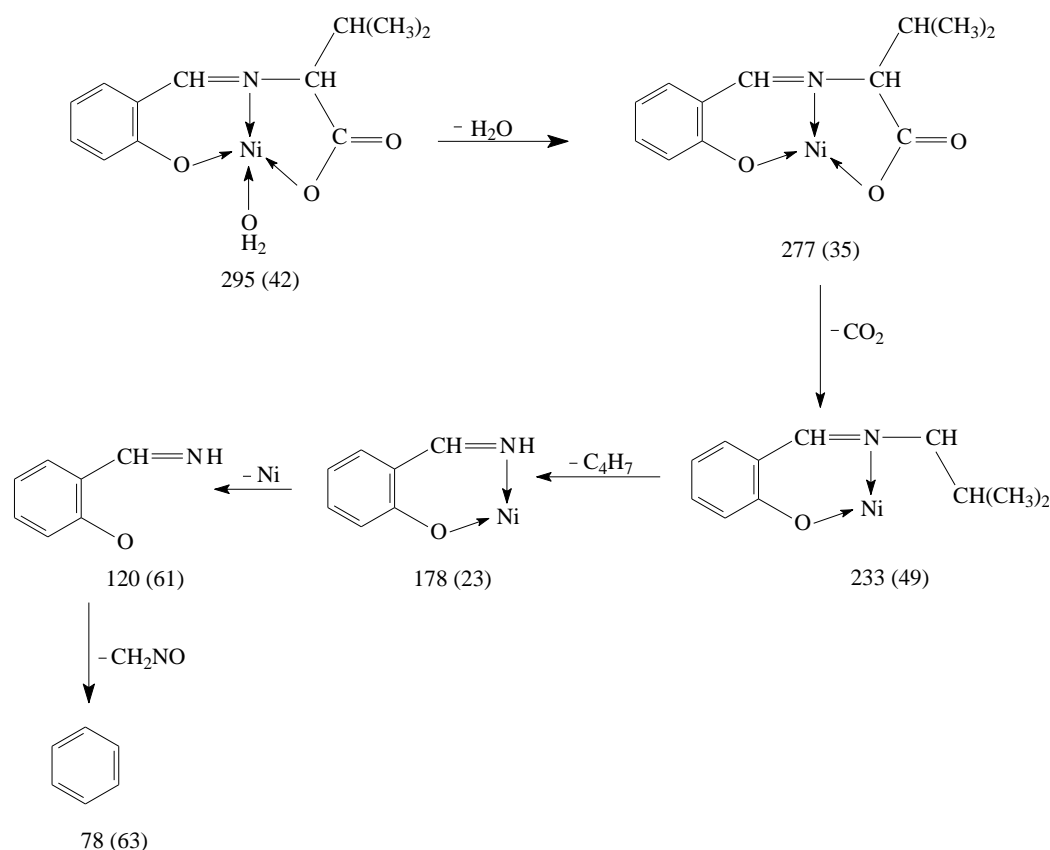
Compound	Colour	Yield (%)	Molar Conductance (S cm <sup>2</sup> mol <sup>-1</sup> )	Analysis, % Found (calcd).			
				C	H	N	Ni
SB C <sub>12</sub> H <sub>15</sub> NO <sub>3</sub>	Bright yellow	55	-	64.89 (65.15)	6.60 (6.78)	6.52 (6.33)	-
NiSB.H <sub>2</sub> O C <sub>12</sub> H <sub>15</sub> NO <sub>4</sub> Ni	Bluish-white	65	0.005	48.49 (48.65)	5.01 (5.06)	4.55 (4.73)	18.22 (19.94)

### Infrared spectra

The infrared spectrum of the free Schiff base shows a band at 1612 cm<sup>-1</sup> due to the formation of imine bond (HC=N-), which is shifted to lower region in the complex implying its involvement in chelation with the metal ion<sup>17,18</sup>. A broad band at 3422 cm<sup>-1</sup> has been assigned to the existence of water molecule<sup>19</sup>. The spectrum also exhibits two bands at 424 and 536 cm<sup>-1</sup> due to  $\nu(\text{Ni-N})$  and  $\nu(\text{Ni-O})$  vibrations, respectively. The appearance of these bands further supports the involvement of azomethine and hydroxyl groups in coordination with Ni(II) ion<sup>20</sup>.

### Mass spectrum of Ni(II) complex

The mass spectrum fragmentation pattern of the Ni(II) Schiff base complex in order to support its structure is given in scheme 1. The observed base peak at  $m/e = 295$  supports the stability of the complex under investigation. A  $H_2O$  molecule is lost from the complex and the same spectrum reveals a peak at  $m/e = 78$  which could be due to the formation of benzene ring.

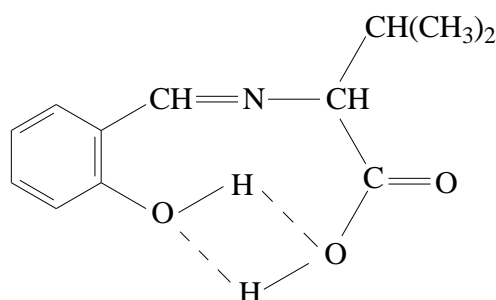


Scheme- 1: Mass spectral fragmentation pattern of the complex

### Electronic spectrum, magnetic moment and Potentiometric studies

Several weak bands are observed in  $13755$  to  $18116\text{ cm}^{-1}$  region in the free ligand corresponding to  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  transitions, implying the presence of phenyl and imine groups, respectively. These weak bands are obscured in the Ni(II) complex due to the presence of strong d-d bands appearing at  $13012$ ,  $17021$  and  $24690\text{ cm}^{-1}$  corresponding to  ${}^3T_1(F) \rightarrow {}^3T_2(F)$ ;  ${}^3T_1(F) \rightarrow {}^3A_2(F)$  and  ${}^3T_1(F) \rightarrow {}^3T_2(F)$  transitions, respectively. The Ni(SB). $H_2O$  complex has a room temperature magnetic moment value of  $2.47\text{ BM}$ . Such a low magnetic moment and electronic spectral data of Ni(SB). $H_2O$  are suggestive of a tetrahedral structure for the NiSB. $H_2O$  complex<sup>21</sup>. The composition of the complex formed in solution was established by measuring the magnitude of the proton displacement during the titration of the Schiff base in absence and presence of metal ions against NaOH. The protonation constant was determined in aqueous medium at  $25$  and  $30\text{ }^\circ\text{C}$ . The titration curve of the Schiff base deviates from free acid curve indicating the release of protons from the ligand. The proton ligand formation number ( $1 < n_A > 1.74$ ) in pH range 3 to 11 indicates the dissociation of two protons. The protonation constant ( $\log K^H$ ) was calculated by Bjerrum<sup>22</sup> and Calvin<sup>23</sup> method as modified by Irving and Rossotti<sup>24</sup>. The protonation constant was found to be  $6.83$  at  $25^\circ\text{C}$  and  $6.34$  at  $30^\circ\text{C}$ . Proton

ligand formation curve was obtained by plotting  $\bar{n}_A$  values against corresponding pH values (fig.1). Since  $\bar{n}_A > 1$ , only  $pK_2$  was evaluated<sup>25</sup>. The possibility of intramolecular hydrogen bonding would perhaps account for the lower  $pK$  value<sup>26, 27</sup> as the hydrogen atom of the hydroxyl group would be less strongly held by oxygen atom (Fig. 1).



**Fig. 1: Intramolecular hydrogen bonding of the Schiff base**

The titration curve of Mn(II), Fe(II), Co(II), Ni(II) and Cu(II) complexes deviate sufficiently from that of free ligand indicating the complex formation. A single inflection point in metal ligand titration curve suggest the formation of only 1:1 complex which is also supported by  $\bar{n}$  value. The metal ligand formation curve was obtained by plotting  $\bar{n}$  values against pL values (Fig. 2). The logK values were determined by point- wise calculation method<sup>22, 23</sup>.

**Table- 2. Stability constants and thermodynamic parameters of the complexes**

Complex	log K		- $\Delta G^\circ$ (KJ/mol)		- $\Delta H^\circ$ (KJ/mol)	$\Delta S^\circ$ (J/Kmol) at 25 °C
	25 °C	30 °C	25 °C	30 °C		
MnSB	9.45	9.24	53.73	53.6	60.3	-22.12
FeSB	9.64	9.49	54.82	55.05	43.06	39.59
CoSB	9.93	9.57	56.4	55.52	103.3	-16.09
NiSB	10.48	10.35	59.6	60.04	37.33	74.9
CuSB	10.06	9.96	57.2	57.7	28.7	95.9

The logK follows the order Mn(II) < Fe(II) < Co(II) < Cu(II) < Ni(II). The stability of Ni(II) complex is exceptionally greater than that of Cu(II) complex. This anomaly has also been observed by Maley and Mellor<sup>28, 29</sup> for metal complexes of leucine and EDTA. Similarly Albert et al.<sup>30</sup> have studied the metal complexes of folic acid but failed to arrive at any definite reason. It was further observed from Table II that the values of stability constants of Mn(II), Fe(II), Co(II), Ni(II) and Cu(II) complexes with Schiff base decrease with rise in temperature.

## Thermodynamic functions

The negative values of  $\Delta G^\circ$  given in Table 2 are indicative of spontaneous reaction between the metal ions and ligand while  $-\Delta H^\circ$  showed the exothermic nature of the metal-ligand interaction. The complex formation is favored at low temperature. The positive values of  $\Delta S^\circ$  obtained in case of Fe(II), Ni(II) and Cu(II) are indicative of chelate formation subsequently stabilizing the complex formation. However, in case of Mn(II) and Co(II) negative values of  $\Delta S^\circ$  may be due to the possible solvent and ligand field interactions.

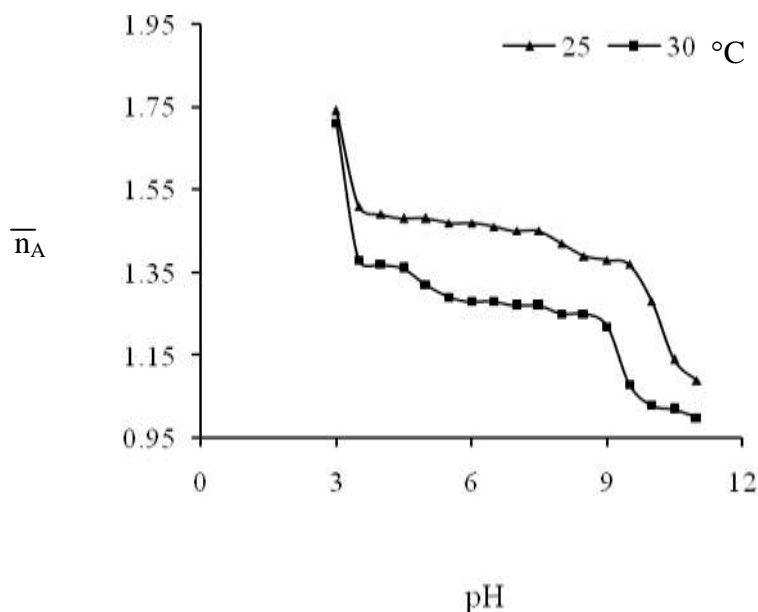
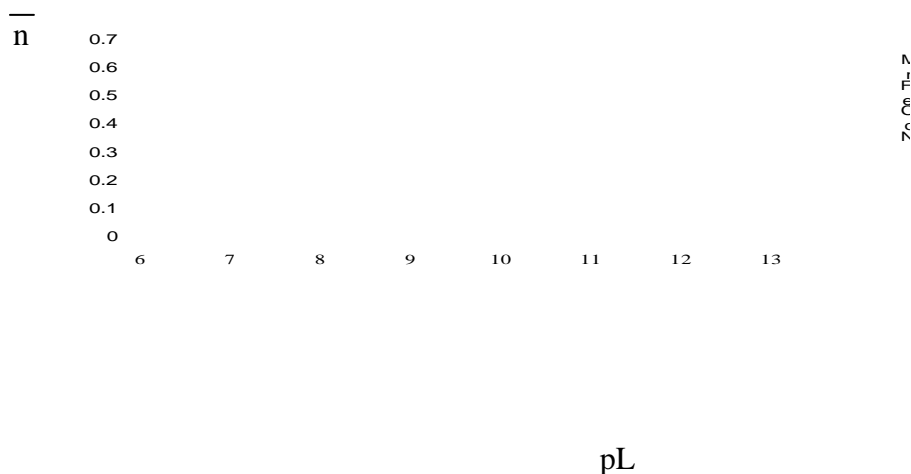


Fig. 2 : Formation curve of the Schiff base



**Fig. 3: Formation curve of bivalent metal complexes with the Schiff base**

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