

# Synthesis, Spectral, Structural determination and electrochemistry of new N<sub>2</sub>O<sub>2</sub> donor Schiff base of transition metal complexes derived from [1-(2-hydroxy-5-methyl-3-nitro phenyl) ethanone-(2S)-2-amino-3-(1H-indol-3-yl) propanoic acid]

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**Abstract :** A novel bidentate Schiff base ligand [1-(2-hydroxy-5-methyl-3-nitro phenyl) ethanone-(2S)-2-amino-3-(1H-indol-3-yl) propanoic acid] was synthesized by the reaction of 1-(2-hydroxy-5-methyl-3-nitro phenyl) ethanone and (2S)-2-amino-3-(1H-indol-3-yl) propanoic acid. The structure of the ligand was elucidated by elemental analysis, IR, H<sup>1</sup>NMR. The cyclic voltammograms of the Mn(II)/Co(II)/Cu(II) complexes investigated in DMSO solution exhibit metal centered electroactivity in the potential range -1.02 to +0.7V. All the complexes showed one electron quasi-reversible redox waves in the voltammogram. The reduction oxidation potential depends on the structure and confirmation of the central metal atom in the co-ordination compounds.

**Index Terms :** Schiff base, elemental analysis, cyclic voltammetry etc.

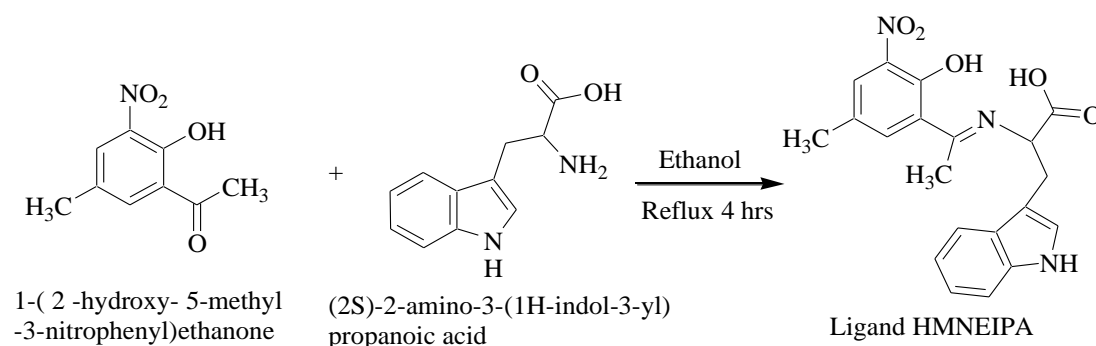
## I INTRODUCTION

Schiff bases have been playing very important role in the development of coordination chemistry. They are prepared by condensing an aldehyde or a ketone and an amine generally in alcohol. Schiff bases have characteristic quality which can stabilize many metals in different oxidation state. Another area of application of these Schiff bases is analytical chemistry where some of these compounds are used as ligand in complexometry topic. The coordination sites of ligands depends on the bonding ability of it, nature of atoms, their electronegativity and steric factor. The lone pair of electrons in either  $\pi$  or  $sp^2$  hybridized nitrogen in the C=N group having the fundamental chemical and biological importance. Cyclic voltammetry has the further attraction of providing information not only on the thermodynamics of redox processes but also on the kinetics of heterogeneous electron-transfer reactions and coupled chemical reactions. The characteristic shapes of the voltammetric waves and their unequivocal position on the potential scale virtually fingerprint the individual electrochemical properties of redox systems. For this reason the method has been labelled "electrochemical spectroscopy" [1].

## II METHODOLOGY

### 2.1 Preparation of [1-(2-hydroxy-5-methyl-3-nitro phenyl) ethanone-(2S)-2-amino-3-(1H-indol-3-yl) propanoic acid] (HMNEIPA).

The Schiff base was synthesized by adding hot ethanolic solution of 1-(2-hydroxy-5-methyl-3-nitro phenyl) ethanone (3.58gm, 0.02M) to a ethanolic solution of (2S)-2-amino-3-(1H-indol-3-yl) propionic acid (4.08gm, 0.02M). The reaction mixture was then refluxed on a water bath for about 4 hours. The condensation product was filtered, washed thoroughly with ethanol and petroleum ether, recrystallized and dried under vacuum. The purity of synthesized compounds was monitored by TLC using silica gel. Yield 68.9%, m.pt. 278°C.



The newly prepared ligand was characterized by elemental analysis, IR and <sup>1</sup>HNMR spectral studies. The elemental analysis for carbon hydrogen and nitrogen is given as follows.

**table no 1: analytical data, color and synthetic condition of ligand hmneipa**

S.N.	Compound	Colour	Time of Reflux (hrs.)	Elemental analysis % found (calcd.)		
				C	H	N
1.	HMNEIPA	orange	4	63.32 (63.18)	4.48 (4.20)	22.16 (22.08)

The ligand HMNEIPA have elemental analysis suggested the empirical formula C<sub>20</sub>H<sub>17</sub>O<sub>5</sub>N<sub>3</sub>.

## 2.2 <sup>1</sup>HNMR spectrum of HMNEIPA (300MHz, CDCl<sub>3</sub> δ in ppm)

The <sup>1</sup>HNMR spectrum of ligand HMNEIPA has been recorded in CDCl<sub>3</sub> which indicated that different non-equivalent protons resonate at different values of applied field. The δ-values in ppm are given below

δ 12.8 (1H, s, phenolic-OH), 8.01 (2H, d, Ar-H), 7.8 (1H, s, Ar-NH), 4.3 (2H, d, -COOH), 3.0 (2H, d, -CH<sub>2</sub>), 3.5 (1H, s, -CH).

## 2.3 Synthesis of Metal Complexes

The metal complexes were complexes by mixing both solution of Schiff base and Metal (II) acetate in DMF-ethanol in molar ratio 2: 1. The resulting solution was refluxed for 4 to 9 hours on water bath. Colored complexes formed have been filtered and then dried in *vacuum*.

All metal complexes are colored, stable in air. The solids do not melt sharply and undergo decomposition. These are insoluble in water and soluble in organic solvent such as DMF and DMSO giving respective colors to the solution.

## III RESULTS AND DISCUSSION

All compounds gave satisfactory elemental analysis. Values are in the close agreement with the values calculated for expected molecular formulae assigned to these complexes, suggesting 1:2

(M:L) stoichiometry. The physical data of ligand and metal complexes are given. (Table 2)

**table no.2: analytical data, color and synthetic condition of complexes of hmneipa**

S. N.	Compound	Color	Solvent	Time (hrs.)	Elemental analysis % found (calcd.)			
					M	C	H	N
1.	[Mn(HMNEIPA) <sub>2</sub> ].2H <sub>2</sub> O	Yellow	DMF+ Ethanol	6	6.85 (6.78)	59.30 (59.18)	3.57 (3.94)	22.28 (22.16)
2.	[Co(HMNEIPA) <sub>2</sub> ].3H <sub>2</sub> O	Light brown	Ethanol	5	7.19 (7.23)	58.70 (58.89)	3.65 (3.92)	20.87 (20.71)
3.	[Ni(HMNEIPA) <sub>2</sub> ].2H <sub>2</sub> O	Pale yellow	Ethanol	6	6.96 (7.01)	59.94 (59.04)	3.98 (3.93)	20.27 (20.61)
4.	[Cu(HMNEIPA) <sub>2</sub> ].2H <sub>2</sub> O	Olive green	DMF+ Ethanol	7	7.87 (7.80)	58.27 (58.53)	3.45 (3.90)	20.26 (20.66)
5.	[Zn(HMNEIPA) <sub>2</sub> ].H <sub>2</sub> O	Brown	Ethanol	6	7.65 (7.91)	58.76 (58.46)	3.97 (3.87)	20.61 (20.46)
6.	[Cd(HMNEIPA) <sub>2</sub> ]	orange	Ethanol	5	12.47 (12.90)	55.10 (55.29)	3.49 (3.48)	19.44 (19.04)

## 3.1 HMNEIPA and its Metal Complexes

The informative and diagnostic IR spectra of the ligand and its respective metal complexes are shown in Table 3. The IR spectrum of the Schiff base exhibits slightly sharp band at 3435 cm<sup>-1</sup> due to intramolecular hydrogen bonded hydroxyl group. [2] This band is absent in all the spectra of complexes indicates the breaking of the hydrogen bond and coordination of oxygen atom to the metal after deprotonation. On further investigation of the bands the strong and sharp band at 1269 cm<sup>-1</sup> due to the ν (C – O)

(phenolic) stretching in the ligand has been shifted to the higher region in the range of 1280 – 1320  $\text{cm}^{-1}$  upon complexation [3]. This shift towards the higher absorption in the complex indicates coordination through the phenolic oxygen .[4] The spectra of almost all the complexes do not show the bands due to  $\nu$  (N - H) and  $\nu$  (C=O) frequencies indicating the coordination of the ligand in its enol form to the metal . The coordinated water molecule is observed in Mn(II), Co(II) and Ni(II) complexes in the regions 3350 – 3460  $\text{cm}^{-1}$ , 1500 – 1531  $\text{cm}^{-1}$  and 817 – 893  $\text{cm}^{-1}$  . The strong band at 1651  $\text{cm}^{-1}$  is assigned to the  $\nu$  (C = N) stretching vibration observed in the ligand and this band shifted lower absorption region in the complexes indicates the participation of the azomethine nitrogen in coordination. The presence of a very strong band in the region of 1525 – 1595  $\text{cm}^{-1}$  is typical for asymmetric vibration of the coordinated carboxylate group, confirms the coordination of the L-tryptophan through the carboxylic oxygen. The band that appears at 1365 – 1367  $\text{cm}^{-1}$  can be ascribed to the symmetric vibration of the coordinated carboxylate . The  $\nu$  (COO)<sub>assy</sub> of carboxylate group of the transition metal complexes were observed in the range of 1573 – 1730  $\text{cm}^{-1}$ . Whereas the  $\nu$  (COO)<sub>sym</sub> is attributed around 1365 – 1460  $\text{cm}^{-1}$  bands is due to coordination with metal to form as ternary complexes. The separation ( $\Delta\nu = \nu_{\text{assy}} - \nu_{\text{sym}}$ ) between  $\nu$  (COO)<sub>assy</sub> and  $\nu$  (COO)<sub>sym</sub> bands of these complexes are consistent with a monodentate coordination of the carboxylate group of L-tryptophan.[5] The N-H stretching frequency of indol ring is not altered in the complexes, hence the –COOH group and indol nitrogen of tryptophan are not involved in the bonding .[6] The coordination through deprotonated phenolic oxygen and nitrogen is further supported by the appearance of new bands at the lower frequency region between 617  $\text{cm}^{-1}$ – 626  $\text{cm}^{-1}$  attributed to  $\nu$  (M - N) and those within the 426 – 472  $\text{cm}^{-1}$  are assigned to  $\nu$ (M – O) .[7]

table 3: infrared spectral data ( $\text{cm}^{-1}$ ) of hmneipa and its metal complexes

S. N.	Compound	$\nu$ (O-H)/ $\nu$ (OH-N)	$\nu$ (COO) <sub>assy</sub>	$\nu$ (COO) <sub>sym</sub>	$\nu$ (C=N)	$\nu$ (NH)	$\nu$ (M-O)	$\nu$ (M-N)	$\nu$ (H <sub>2</sub> O)
01	HMNEIPA	3435	1573	1365	1651	3172	--	--	--
02	[Mn(HMNEIPA) <sub>2</sub> ].2H <sub>2</sub> O	--	1651	1421	1531	3135	624	472	3350
03	[Co(HMNEIPA) <sub>2</sub> ].3H <sub>2</sub> O	--	1654	1442	1502	3113	623	418	3442
04	[Ni(HMNEIPA) <sub>2</sub> ].2H <sub>2</sub> O	--	1651	1417	1558	3137	624	482	3450
05	[Cu(HMNEIPA) <sub>2</sub> ].2H <sub>2</sub> O	--	1730	1460	1525	3164	626	437	3460
06	[Zn(HMNEIPA) <sub>2</sub> ].H <sub>2</sub> O	--	1653	1425	1525	3164	617	426	3398
07	[Cd(HMNEIPA) <sub>2</sub> ]	--	1627	1421	1529	3100	621	430	

table 4: electronic and magnetic spectral data of complexes of hmneipa

Sr. No.	Ligand	$\mu_{\text{eff}}$ B.M.	Absorption band		Assignments
			(nm)	( $\text{cm}^{-1}$ )	
1	[Mn(HMNEIPA) <sub>2</sub> ].2H <sub>2</sub> O	6.30	563	17761	${}^6A_{1g} \rightarrow {}^4T_{1g}$ (4G)
			412	24271	${}^6A_{1g} \rightarrow {}^4T_{2g}$ (4G)
			375	26666	${}^6A_{1g} \rightarrow {}^4E_g$
2	[Co(HMNEIPA) <sub>2</sub> ].3H <sub>2</sub> O	4.70	745	13422	${}^4A_2 \rightarrow {}^4T_1$
			599	16694	${}^4A_2 \rightarrow {}^4T_1$ (F)
			382	26178	C.T.
3	[Ni(HMNEIPA) <sub>2</sub> ].2H <sub>2</sub> O	2.80	838	11933	${}^3A_{2g}$ (F) $\rightarrow$ ${}^3T_{1g}$ (F)
			785	13605	${}^3A_{2g} \rightarrow {}^3T_{2g}$

			420	23809	$^3A_{2g}(F) \rightarrow ^3T_{1g}(F)$
4	$[Cu(HMNEIPA)_2] \cdot 2H_2O$	1.80	720 586 522	13888 17064 19157	$^2B_{2g} \rightarrow ^2A_{1g}$ $^2B_{1g} \rightarrow ^2E_g$ C.T.
5	$[Zn(HMNEIPA)_2]H_2O$	Diamagnetic	-	-	-
6	$[Cd(HMNEIPA)_2]$	Diamagnetic	-	-	-

### 3.2 Cyclic voltammetric analysis of metal complexes of HMNEIPA:

The Mn(II)–HMNEIPA complex shows two reduction oxidation prominent waves at positive and negative potential at  $E_{pa} = 0.186$  V,  $-0.777$  V and  $E_{pc} = -0.087$  V,  $-0.828$  V respectively. The first wave of redox potential with  $\Delta E = 0.099$  V. This process is consistent with one electron irreversible redox couple  $Mn(II) \rightarrow Mn(I)$ . The second wave is reversible at  $\Delta E = 0.052$  V [8]  $Mn(I) \leftrightarrow Mn(0)$ . This redox process is attributed to ligand base [9].

The cyclic voltammetric curves of cobalt(II) complex of HMNEIPA showed two reduction potential, among these first reduction potential occurs at  $E_{pc} = -0.602$  V at cathodic peak having  $\Delta E = 0.119$  V which shows that quasi-reversible two electron reduction as  $Co(II) \rightarrow Co(0)$  from the current peak ration value. This reduction attribute to metal base reduction and second redox potential occurs cathodic peak potential at  $E_{pc} = -1.306$  V is associated with anodic peak potential at  $E_{pa} = -1.207$  V. But the redox process is purely irreversible one electron process which is ligand base. This value assigned to  $Co(II) \rightarrow Co(I)$  and  $Co(II) \rightarrow Co(III)$  respectively.

The cyclic voltammetric curves for the electrochemical reduction of the studied copper (II) complexes exhibit a redox couple in the range of  $-0.131$  V to  $-0.774$  V between them two reduction waves occurs in the voltammogram which can be attributed to the reduction of the metal center. [10,11] For the Cu(II) complex when the ratio of  $i_{pa}/i_{pc}$  takes place close to one the process will be reversible or quasi-reversible but out of both reduction couple, no one potential is reversible or quasi-reversible. So Cu(II) complex gives irreversible two electron reduction potential.  $Cu(II) \rightarrow Cu(0)$  for metal center.

table 5: electrochemical data of metal complexes of hmneipa

Complexes of HMNEIPA	$E_{pc}^1$ (V)	$E_{pa}^1$ (V)	$E_{1/2}$ (V)	$\Delta E$ (V)	$E_{pc}^2$ (V)	$E_{pa}^2$ (V)	$E_{1/2}$ (V)	$\Delta E$ (V)
Mn(II)	0.087	0.186	-0.136	0.099	-0.828	-0.777	-0.802	0.051
Co(II)	-0.602	-0.483	-0.542	0.119	-1.306	-1.207	-1.256	0.058
Cu(II)	-0.131	0.037	-0.084	0.168	-0.774	-0.67	-0.722	0.104

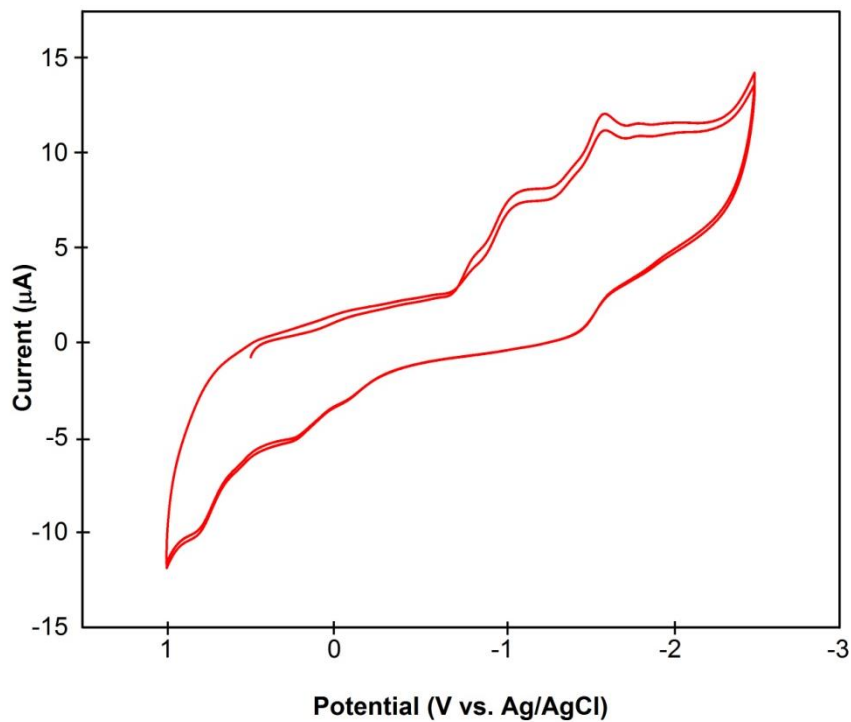


fig. 1: cyclic voltammogram of mn(ii) complex of hmneipa

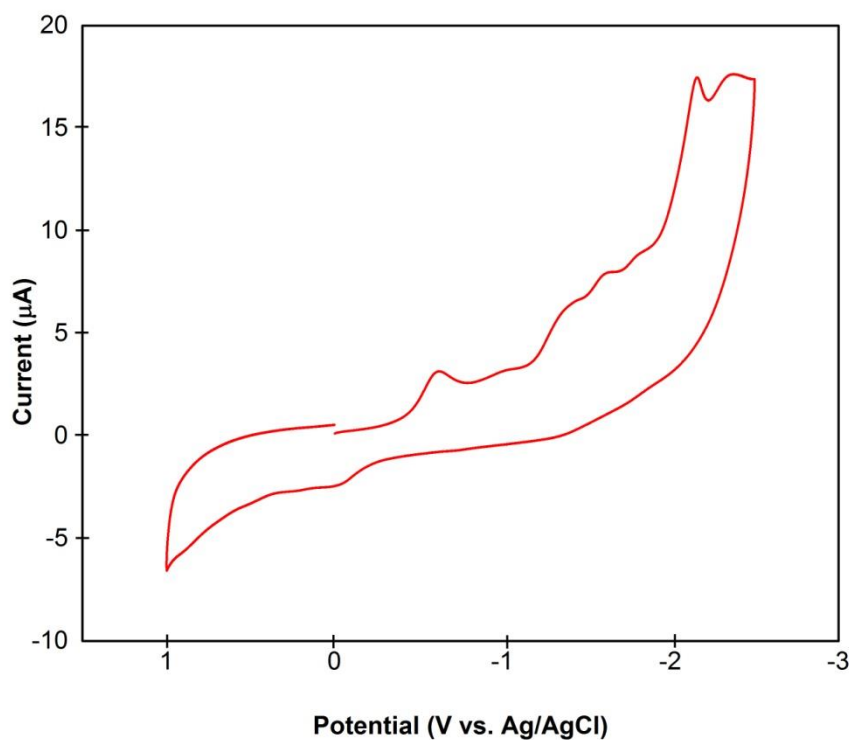


fig. 2: cyclic voltammogram of co(ii) complex of hmneipa

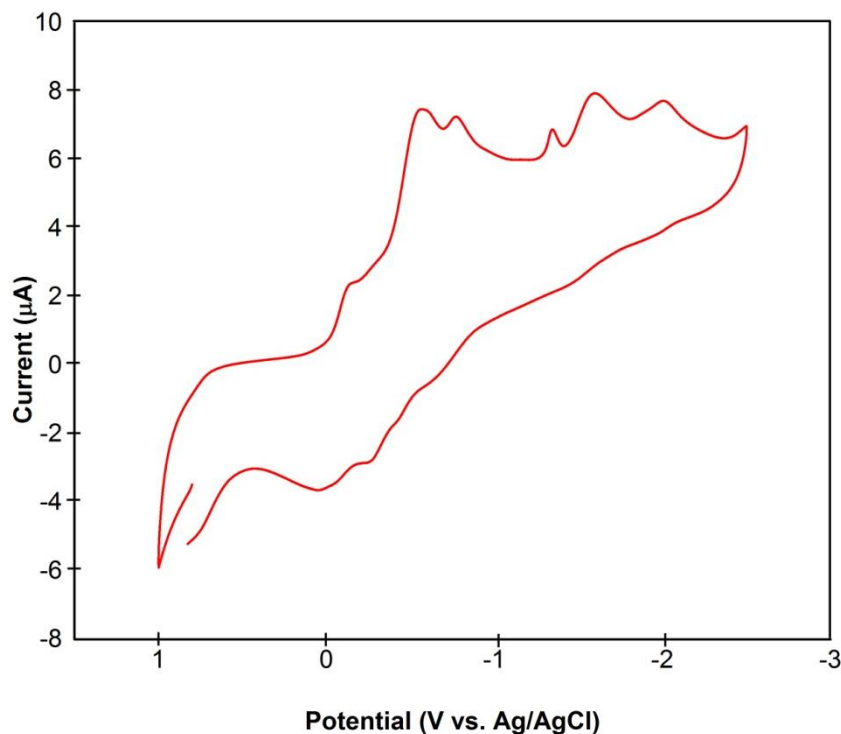


fig. 3: cyclic voltammogram of cu(ii) complex of hmneipa

#### IV CONCLUSION

The cyclic voltametry is usually employed to study the redox behaviour of metal complexes of Mn(II), Co(II) and Cu(II) with Schiff base ligand. In the present course of study reduction and oxidation potentials were measured from the voltammogram. The values of  $\Delta E$  and  $E_{1/2}$  (Potential difference and half potential respectively) calculated from their respective voltammogram. The values are obtained by plotting a graph current against potential.

The metal complexes of Mn(II), Co(II) and Ni(II) were studied by using this property because of these complexes showed variable valences due to this we could observed the redox property clearly (more than one electron transferred). From this study oxidation states of metals were confirmed also. Some of the metal ions showed with different ligand the redox behaviour such as weather it may be reversible, quasi reversible and irreversible.

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