



SYNTHESIS AND EVALUATION OF THE SEMICONDUCTING BEHAVIOR IN THE COMPLEXES OF SCHIFF BASE LIGAND-*DHPEAHP*

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ABSTRACT

Schiff bases derived from an amino acid are an important class of ligands that coordinate to metal ions via azomethine nitrogen and have been studied extensively. Schiff-base complexes are considered to be among the most important stereochemical models in main group and transition metal coordination chemistry due to their preparative accessibility and structural variety. The amino acid ligand [1-(2,4-dihydroxy-phenyl)-ethanone-(S)-alpha-amino-4-hydroxybenzenepropanoic acid] was prepared by the reaction of 1-(2,4-dihydroxy-phenyl)-ethanone with (S)-alpha-amino-4-hydroxybenzene propanoic acid. The complexes of this ligand have been prepared using metal acetates of Mn(II), Co(II), Ni(II), Cr(III), Cu(II), Zn(II) and Cd(II) under reflux in methanol. The products were found to be crystalline solid. The complexes have been characterized by analytical, ¹HNMR, FT-IR and diffused reflectance spectral studies. The solid state electrical conductivity has been measured over 40–130 °C temperature range and all the compounds showed semiconducting behavior as their conductivity increases with increase in temperature.

Key words: Amino acid, spectral studies, stereochemical models semiconducting nature, etc.

INTRODUCTION

Schiff bases with N₂O₂ donor atoms are well known to coordinate with various metal ions and have attracted a great deal of interest in recent years due to their potential ligating ability, structural flexibility, spectral and chemical properties as well as magnetic properties[1-2]. Schiff bases and their metal complexes exhibit a broad range of potential applications because of their structural diversity and intrinsic magnetic properties and have shown to be potential antibacterial and anticancer agents. Schiff base complexes are also important for designing metal complexes related to synthetic and natural oxygen carriers.² The complexes make these compounds effective and stereospecific catalysts for oxidation, reduction and hydrolysis and they show biological activity, and other transformations of organic and inorganic chemistry [3].

Extensive investigations have been made on acetophenone amino acid Schiff bases and their metal complexes because of their possible use as potential N-pyridoxylidene amino acid systems. Metal chelates of the Schiff bases derived from acetophenone and amino acids have been shown to be important class of compounds in elucidating the mechanism of transamination reaction. Amino acid Schiff bases are sensitive to moisture and decompose when exposed to air, hence they are usually generated immediately prior to use for complexation. This is because only a small number of crystalline Schiff bases derived from amino acids and acetophenone can be isolated. In this work we report the synthesis and electrical studies of Schiff base derived from the

condensation of (*S*)- α -amino-4-hydroxybenzenepropanoic with [1-(2,4-dihydroxy-phenyl)-ethanone] and their metal complexes with Mn(II), Co(II), Ni(II), Cr(III), Cu(II), Zn(II) and Cd(II) ions.

MATERIALS AND METHODS

All the chemicals were of A.R. grade and used as received. 1-(2,4-dihydroxy-phenyl)-ethanone was prepared by known methods. The solvents were purified by standard methods. IR spectra of the compounds were recorded on Perkin Elmer 842 spectrophotometer in the region 400-4000 cm^{-1} . The diffuse reflectance spectra of the complexes were recorded on Varian Cary-5000 UV-visible spectrophotometer. The thermogravimetric analysis was performed in air atmosphere at 10⁰ C min⁻¹ heating rate. ¹H-NMR was acquired with BRUKER-400 spectrometer in DMSO-d⁶. Elemental microanalysis were performed on a (C.H.N) analyser from heraeus (Vario EL). The chloride contents for complexes were determined by using potentiometer titration method on (686-Swiss).

EXPERIMENTAL SECTION

A. Synthesis of [1-(2,4-Dihydroxy-phenyl)-ethanone-(*S*)-Alpha-amino-4-hydroxybenzenepropanoic acid][DHPEAHP] :

[1-(2,4-Dihydroxy-phenyl)-ethanone] (1.52 gm, 0.01mmole) and (*S*)-Alpha-amino-4-hydroxybenzenepropanoic acid (1.81gm, 0.01mmole) were placed in round bottomed flask in distilled methanolic medium, and few drops of acetic acid were added as a catalyst. The reaction mixture was refluxed on water bath for 3.5 hr and then poured on crushed ice to get yellow-orange crystals of Schiff base ligand DHPEAHP. The precipitated crystals of Schiff base were filtered and recrystallised with aqueous ethanol and dried. The yield was found to be 69.34%. Following Scheme represents synthesis of ligand.

B. Preparation of metal complexes:

All the complexes were prepared by mixing a ethanolic solution of $\text{M}(\text{CH}_3\text{CO})_n \cdot n\text{H}_2\text{O}$ with the methanolic solution of Schiff base DHPEAHP in a 1:1 molar ratio. The resulting mixture was refluxed on a water bath for 8–9 h. A colored product appeared on standing and cooling the solution. The precipitated complex was then filtered under suction and washed successively with hot water and methanol to remove unreacted ligand and metal acetate if any present and then dried.

RESULTS AND DISCUSSION

The ligand DHEPEAHP and its complexes have been characterized on the basis of ¹H NMR, IR spectral data, elemental analysis, diffused reflectance spectra, electrical conductance, magnetic susceptibility measurements and thermogravimetric analysis data.

The tridentate *ONO* donor hydrazone ligand used in the present work was derived from the condensation of [1-(2,4-Dihydroxy-phenyl)-ethanone with (*S*)-Alpha-amino-4-hydroxybenzenepropanoic acid in ethanol. The elemental analyses [Table 1] indicate that all these complexes have 1:1 metal: ligand stiochiometry.

Table 1: Analytical data, color and synthetic conditions of complexes of DHPEAHP

S. N.	Compounds	Color	Solvent used	Time of Reflux (hrs.)	Elemental analyses % found (calcd.)			
					M	C	H	N
1.	[Cr(DHPEAHP)(H ₂ O) ₃]. H ₂ O	Apple Green	DMF-EtOH	8	12.05 (11.89)	46.47 (46.68)	5.18 (5.30)	3.47 (3.29)
2.	[Mn(DHPEAHP)(H ₂ O) ₃]	Pale rose	EtOH	6	13.21 (13.02)	48.53 (48.35)	5.23 (5.00)	3.12 (3.33)
3.	[Co(DHPEAHP)(H ₂ O)]	Candy	EtOH	6	15.28 (15.10)	54.12 (52.32)	4.21 (4.40)	4.22 (4.00)
4.	[Ni(DHPEAHP)(H ₂ O) ₃]	Pale Green	DMF-EtOH	5	14.00 (13.78)	47.66 (47.93)	4.78 (4.98)	3.30 (3.42)
5.	[Cu(DHPEAHP)(H ₂ O)]. 2H ₂ O	Olive Green	DMF-EtOH	10	14.54 (14.75)	47.70 (47.39)	4.61 (4.92)	3.42 (3.25)
6.	[Zn(DHPEAHP)(H ₂ O)]	Light Brown	EtOH	8	16.30 (16.48)	51.60 (51.47)	4.14 (4.32)	3.45 (3.53)
7.	[Cd(DHPEAHP)(H ₂ O)]. H ₂ O	Pale Orange	EtOH	8	24.15 (24.35)	44.04 (44.22)	4.25 (4.15)	3.28 (3.03)

¹H NMR spectrum of DHPEAHP (300MHz, CDCl₃, δ in ppm):

The ¹H NMR spectrum of ligand DHPEAHP has been recorded in CDCl₃, which indicated that different non-equivalent proton(s), resonates at different values of applied field. The δ-values in ppm are given below:

12.67 (1H, broad, s, phenolic -OH), 11.85 (1H, s, -NH), 7.65-6.37 (7H, m, Ar-H), 4.82 (1H, t, -CH), 2.56 (2H, d, -CH₂), 1.602 (3H, s, -CH₃).

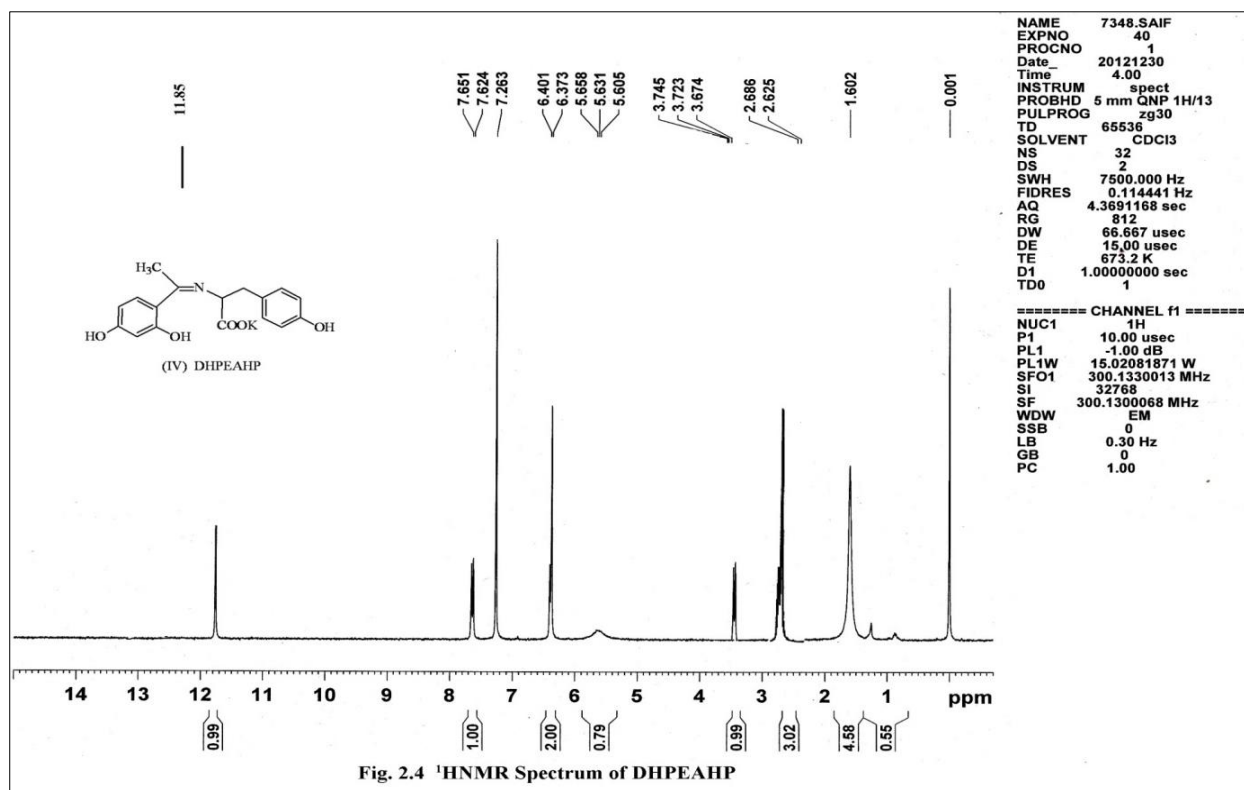


Fig.1: ¹H NMR spectrum of DHPEAHP

INFRARED SPECTRA

The azomethine and carboxylate bands in the IR spectra of the complexes appear in the range 1599 – 1633, 1582 – 1589 and 1392 – 1410 cm^{-1} , somewhat lower than observed for the free ligands. These indicate that the azomethine nitrogen and the oxygen of the carboxylate group are coordinated to metal ion[4].

The IR spectra of all complexes display a band at 3420-3226 cm^{-1} which attributed to $\nu(\text{OH})$ of water molecules. The presence of bands at 1544-1514 cm^{-1} and ~860-800 cm^{-1} in the spectra of aqua complexes attributed to the $\nu(\text{H}_2\text{O})$ and (OH) rocking vibration respectively suggesting coordinate nature of water molecules[5-6].

Table 2: Infrared spectral data (cm⁻¹) of DHPEAHP and its metal complexes.

S.N.	Compounds	$\nu(\text{O-H})/\nu(\text{OH-N})$	$\nu(\text{COO})$ assy	$\nu(\text{COO})$ sym	$\nu(\text{C-O})$	$\nu(\text{C=N})$	$\nu(\text{M-O})$	$\nu(\text{M-N})$	$\nu(\text{H}_2\text{O})$
1.	DHPEAHP	3398	1678	1428	1300	1632	--	--	--
2.	[Mn(DHPEAHP)(H ₂ O) ₃]	--	1610	1414	1310	1600	465	536	3226, 1516, 848
3.	[Co(DHPEAHP)(H ₂ O)]	--	1614	1400	1302	1608	470	534	3420, 1524, 864
4.	[Ni(DHPEAHP)(H ₂ O) ₃]	--	1623	1396	1312	1604	468	524	3258, 1514, 806
5.	[Cr(DHPEAHP)(H ₂ O) ₃] (H ₂ O)	--	1598	1394	1312	1598	480	512	3346, 1544, 804
6.	[Cu(DHPEAHP)(H ₂ O)] 2(H ₂ O)	--	1604	1398	1308	1602	478	546	3214, 1530, 826
7.	[Zn(DHPEAHP)(H ₂ O)]	--	1615	1394	1306	1604	472	525	3326, 1522, 810
8.	[Cd(DHPEAHP)(H ₂ O)] (H ₂ O)	--	1600	1390	1318	1614	477	538	3344, 1526, 804

Electrical Conductivity Studies

From the results of temperature dependence of electrical conductivity of DHPEAHP and its complexes it is seen that,

1. Electrical conductivity of complexes of DHPEAHP at room temperature lies in the range 1.68×10^{-6} - $2.40 \times 10^{-5} \Omega^{-1} \text{cm}^{-1}$, suggesting their semiconducting nature
2. The room temperature electrical conductivity decreases in the order Co(II) > Cr(III) > Cd(II) > Ni(II) > Mn(II) > Cu(II) > Zn(II). The plots of $\log \sigma$ against $1/T$ are linear in studied temperatures, therefore, it may be concluded that these metal complexes shows semiconducting nature [7-8].
3. However, at low temperature the variation of electrical conductivity with metal ions i.e. Co(II), Cr(III) and Cu(II) is not much significant. However, at high temperature, the conductivity varies significantly, which may be due to intrinsic conduction [9-10].
4. The activation energy of electrical conduction of complexes of DHPEAHP lies in the range 0.52-1.434 eV and decreases in the order Co(II) > Mn(II) > Cr(III) > Cd(II) > Zn(II) > Cu(II) > Ni(II).

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