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Synthesis and Characterization of Transition Metal Complexes of N, O Chelating Schiff Base Ligand Bis-[(1-(5-Chloro-2-Hydroxyphenyl) -Ethanone-Diaminopropane]

Abdul Wajid* and Rahul B. Mohod

P. G. Department of Chemistry, Shri Shivaji College of Arts, Commerce and Science, Akola-444 001(M.S.) India.

*Corres.author: wajidabdul871@gmail.com Phone no.07385775506

Abstract: The ligand CHPEDAP, a condensation product of 1-(5-chloro-2-hydroxyphenyl) ethanone and 1, 3 diaminopropane, was synthesized and its coordination behavior with Mn(II), Co(II), Ni(II), Cr(III),Cu(II), Zn(II) and Cd(II) ions was investigated by isolating and elucidating the structure of the complexes by spectral (IR, ¹H NMR and diffuse reflectance), magnetic susceptibility and electrical conductivity measurement . The ligand acts as tetradentade in case of all complexes with N, O donor sites. The DC electrical conductivity was measured over a wide range of temperature in its pellet form.

Key words: CHPEDAP, magnetic susceptibility, DC electrical conductivity.

Introduction

The Schiff bases play a significant role in the area of coordination chemistry. They have been widely studied because of their industrial and biological applications. Schiff bases are usually formed by the condensation of aliphatic or aromatic, aldehydes or ketones with primary aliphatic or aromatic amines, hydrazides, etc. The significance of Schiff bases like azomethines, hydrazones, semicarbazones, thiosemicarbazones, etc., lies in the fact that these compounds not only possess antimicrobial activities but also show greater tendency to form complexes [1]. Transition metal complexes with Schiff base as ligand have been amongst the widely studied coordination compounds in the past few years, since they are found to be widely applicable in many field like biochemical, analytical and anti microbial fields [2-5]. A novel Schiff base ligand derived from 1-(5-chloro-2-hydroxyphenyl)ethanone and 1, 3diaminopropane and its transition metal complexes with different metal acetates were prepared and their spectral properties [6] were investigated. Hence it was thought of interest to study the reactions of this Schiff base [CHPEDAP] and its metal complexes with Mn(II), Co(II), Ni(II), Cr(III), Cu(II), Zn(II) and Cd(II) metal ions.

Experimental

All the chemicals were of A.R. grade and used as received. 1-(5-chloro-2-hydroxyphenyl) ethanone was prepared by known methods [7-10]. The solvents were purified by standard methods [11].

The ¹H NMR spectra of ligand was obtained from microanalytical unit. IR spectra of the compounds were recorded on Perkin Elmer 842 spectrophotometer in the region 400-4000cm⁻¹. The diffuse reflectance spectra of

the complexes were recorded on Varian Cary-5E UV-visible spectrophotometer. The magnetic moment measurement were made on a Gouy balance at room temperature using $Hg[Co(SCN)_4]$ as the celebrant.

Preparation of Schiff base ligand [CHPEDAP]

To the solution of 1-(5-chloro-2-hydroxyphenyl) ethanone (25ml, 0.02M) in ethanol, 1, 3 diaminopropane was added (2:1) drop wise and the reaction mixture was refluxed on a water bath for 4 hours. After cooling a pale yellow colored crystalline solid was separated out. It was filtered and washed with ethanol, crystallized from DMF and dried under reduced pressure at ambient temperature. The purity of ligand was checked by elemental analysis and m.p. It was also characterized by IR and ¹H NMR spectral studies. Yield of CHPEDAP: 61%.



ethanone

bis[1-(5-Chloro-2-hydroxy-phenyl)-ethanone -diaminopropane]

¹H NMR (300 MHz, CDCl₃, in ppm)

The ¹H NMR spectra of ligand were recorded in $CDCl_3$ at 300 MHz on a Bruker DRX-300 NMR spectrometer with TMS as an internal reference.

6.75-7.04 (6H, m, Ar-H), 1.65 (2H, s(b) -OH), 2.34 (6H, s, -CH₃), 3.65-3.76 (4H, t, -CH₂).

Preparation of metal complexes

All the metal complexes were prepared in a similar way by following method.

To a hot solution of ligand [CHPEDAP] (0.02M) in 25ml of ethanol a suspension of respective metal salts [acetates of with Mn(II), Co(II), Ni(II), Cr(III),Cu(II), Zn(II) and Cd(II)] was added drop wise with constant stirring. The reaction mixture was refluxed on a water bath for 4-11 hours. The precipitated complexes were filtered, washed with ethanol followed by ether and dried over fused calcium chloride. Yield: 45-50%.

Results and Discussion

<u>FT Infrared Spectra (KBr, € in cm⁻¹)</u>

IR spectra of ligand and metal complexes shows v(C=N) peaks at 1612 cm⁻¹ and absence of C=O peak at around 1700-1800 cm⁻¹ indicate Schiff base formation. The structurally important vibration bands of the free ligands and their metal complexes which are useful for determining the mode of coordination of the ligand are given in Table 2. The CHPEDAP exhibits a medium intense band at 2922-2925 cm⁻¹ due to the intramolecular hydrogen bonded (O-H) [12]. The absence of this band in the spectra of complexes indicates deprotonation of the phenolic group and coordination of the oxygen atom to the metal ion. The strong band in the region 1612–1651 cm⁻¹ region may be assigned to the (C=N) (azomethine). In this region, the C=N band may not be pure and it may be associated with the aromatic (C=C) stretching band. Shifting of this band to a lower wave number by 20–40 cm⁻¹ in the metal complexes in comparison to the free ligands indicates the coordination of azomethine nitrogen to the metal [13]. The presence of new bands in the spectra of complexes in the range 515–679 cm⁻¹ is attributed to M–N and M–O modes respectively [14].

Magnetic and Electronic study

The room temperature magnetic moment of Mn(II) complex is 5.98 B.M. suggesting octahedral geometry to the complex [15-17]. The Mn(II) complex shows three bands at 17301, 22988 and 25974 cm⁻¹. These spectral bands are assigned as to the ${}^{6}A_{1g} \rightarrow {}^{4}T_{1g}$ (${}^{4}G$), ${}^{6}A_{1} \rightarrow {}^{4}T_{1g}$ (${}^{4}G$) and ${}^{6}A_{1} \rightarrow {}^{4}T_{1g}$ (${}^{4}Eg$) transitions, respectively towards octahedral structure around Mn(II) ion. The Co(II) complex shows magnetic moment 4.75 B.M. suggest high spin octahedral geometry for Co(II) complex . The electronic spectrum Co(II) complex shows three bands in the regions 7812, 10050 and 16722 cm-1 assignable to ${}^{4}T_{1g}(F) \rightarrow {}^{4}T_{2g}(F)$, ${}^{4}T_{1g}(F) \rightarrow {}^{4}A_{2g}(F)$ and ${}^{4}T_{1g}(F) \rightarrow {}^{4}T_{1g}(P)$ transitions respectively in an octahedral environment around the cobalt ion. The magnetic moment of Ni(II) complex is 2.86 B.M. which lies in the normal range of octahedral Ni(II) complexes. The electronic spectrum of Ni(II) complex exhibits three bands at 10559, 17543 and 25188 cm⁻¹. These bands may be assigned to the transitions ${}^{3}A_{2g}(F) \rightarrow {}^{3}T_{2g}(F)$, ${}^{3}A_{2g}(F) \rightarrow {}^{3}T_{1g}(F)$ and ${}^{3}A_{2g}(F) \rightarrow {}^{3}T_{1g}(P)$ transitions respectively in octahedral configuration[18-19]. The Cr(III)complex has magnetic moment value 3.79 B.M. which is in good agreement reported for octahedral Cr(III) complexes. The electronic spectrum of this complex exhibits three bands at 14947, 20000 and 31840cm⁻¹ which indicates ${}^{4}A_{2g} \rightarrow {}^{4}T_{1g}(P)$, ${}^{4}A_{2g} \rightarrow {}^{4}T_{1g}(F)$ and ${}^{4}A_{2g} \rightarrow {}^{4}T_{2g}(F)$ transitions respectively. The observed magnetic moment of Cu(II) complex is found to be 1.89 B.M. suggesting distorted octahedral geometry. The Cu (II) complex shows bands at 17301, 19455 and 20920 cm-1 due to ${}^{2}B_{1g}$ $\rightarrow^2 A_{1g}$, $^2 B_{1g} \rightarrow^2 B_{2g}$ and $^2 B_{1g} \rightarrow^2 E_g$ transitions respectively towards pseudo octahedral structure around Cu(II) ion [20]. The Zn(II) and Cd(II) complexes are found diamagnetic as expected from their electronic configurations and may have tetrahedral geometry [21].

Electrical Conductivity

The temperature dependence of the solid state electrical conductivity (σ) of the complex in their compressed pellet form have been measured in the temperature range 313-430 K using two probe method. The electrical conductivity and activation energy values are given in the Table1.

S.N.	Compound	Color	Electrical conductivity Ω^{-1} cm ⁻¹ at 373K	Activation energy in eV
1.	[Mn(CHPEDAP).2H ₂ O]	Cairo Bazaar	7.71 x 10 ⁻⁶	1.06
2.	[Co(CHPEDAP).2H ₂ O]	Grayish Brown	9.90 x10 ⁻⁵	0.97
3.	[Ni(CHPEDAP).2H ₂ O]	Sapphire Ice	3.14 x10 ⁻⁸	0.84
4.	[Cr(CHPEDAP).2H ₂ O]	Graish Green	3.17×10^{-8}	0.94
5.	[Cu(CHPEDAP).2H ₂ O]	Raven Song	2.84×10^{-3}	0.79
6.	[Zn(CHPEDAP). 2H ₂ O]	Lemon Pie	$1.92 \text{ x} 10^{-3}$	0.81
7.	[Cd(CHPEDAP).2H ₂ O]	Day Break	$4.16 \text{ x} 10^{-4}$	0.74

Table1: Electrical conductivity data of CHPEDAP complexes

It was found that the electrical conductivity values increases with increase in the temperature according to the relation [22] $\sigma = \sigma_0 \exp$ (-Ea/RT), where Ea represents the ordering activation energy of the conduction process and σ_0 is constant. The plot of log σ vs. 1/T are found to be linear in studies temperature range 313-398 K indicating semiconducting nature [23]. The electrical conductivity of the complexes at 373 lies in the range of 3.14 x 10⁻⁸ to 1.92 x10⁻³ Ω^{-1} cm⁻¹. The activation energy of the complexes at 373 K decreases in the order Cd(II)>Cu(II)>Cn(II)>Cr(III)>Co(II)>Mn(II).

Conclusion

IR spectrum reveals that the ligand [CHPEDAP] coordinates in a tetradentate manner involving NNOO. The newly synthesized complexes namely [Mn(CHPEDAP).2H₂O],[Co(CHPEDAP).2H₂O], [Ni(CHPEDAP).2H₂O], [Cr(CHPEDAP).2H₂O] possess octahedral geometry, [Cu(CHPEDAP).2H₂O] shows distorted octahedral geometry while [Zn(CHPEDAP).2H₂O] and [Cd(CHPEDAP).2H₂O] possess tetrahedral geometry.

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