

SYNTHESIS AND ELECTRICAL CONDUCTIVITY STUDY OF SOME NOVEL N,O-DONOR SCHIFF BASE METAL COMPLEXES

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Abstract:

The complexes of Mn(II), Co(II), Ni(II), Cr(III), Cu(II), Zn(II) and Cd(II) with the chelating ligand derived from [1-(5-chloro-2-hydroxyphenyl)ethanone] and 2-chloropyridine-3-carboxamide have been synthesized. The chelates have been characterized on the basis of elemental analyses, IR, ¹HNMR, magnetic moment, electronic spectral data. 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. The complexes are colored and stable in air at room temperature. The structure of the ligands were elucidated by spectral studies which indicate the presence of two or three coordinating groups in ligands which may be oxygen atom of the phenolic -OH group, the nitrogen atom of the azomethine (C=N) group and the oxygen atom of the carbonyl group.

Keywords: 2-chloropyridine-3-carboxamide, d c electrical conductivity, Azomethine linkage.

I. INTRODUCTION

The most important problems of present day chemistry is the creation of new substances and materials possessing a series of valuable properties. Particularly great prospects have been opened up in the synthesis and study of organic compounds having delocalized electrons because of the presence of conjugated bonds in them or the formation of complexes. Such compounds have acquired the name, organic semiconductors [1,2]. At the present time organic semiconductors include low molecular weight compound like aromatic dyes and phthalocyanines, polymers with a large number of conjugated bonds, charge transfer complexes, stable free radicals and some biopolymers whose conductivity can be explained by non-ionic behaviour [3-4]. Various studies have shown that Schiff base derived from substituted acetophenone containing nitrogen/sulphur and/or oxygen as ligand atoms are of interest as simple structural models of more complicated biological systems [5, 6] and their metal complexes shown wide spectrum of application such as biochemical, analytical, industrial and antimicrobial agents [7]. In the present paper, we report the synthesis and electrical conductivity of complexes derived from [1-(5-chloro-2-hydroxyphenyl)ethanone] and 2-chloropyridine-3-carboxamide.

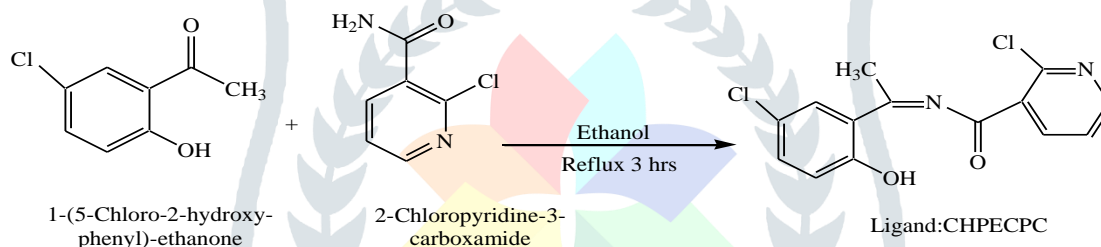
II. MATERIALS AND METHOD

Manganese(II), cobalt(II), nickel(II), chromium(III), copper(II), zinc(II), and cadmium(II) acetate salts used were of Merck and BDH make. Organic solvents such as absolute ethanol, methanol, petroleum ether, dimethylformamide (DMF) and dimethylsulfoxide (DMSO) were of AR grade. from [1-(2,4-dihydroxyphenyl)ethanone] was prepared by known methods. Elemental microanalysis was performed on a (C.H.N.) analyser from heraeus (Vario EL). IR spectra of the compounds were recorded on Perkin Elmer 842 spectrophotometer in the region $400\text{-}4000\text{cm}^{-1}$. $^1\text{H-NMR}$ spectrum of the ligand was recorded in DMSO-d₆ on a Bruker DRX-300 FTNMR spectrometer. Solid-state electrical conductivity of complexes was measured in their compressed pellet forms using conventional two-probe method.

III. EXPERIMENTAL

Synthesis of Schiff base ligand [CHPECPC] and its complexes

The Schiff base was synthesized by adding an ethanolic solution of 1-(5-chloro-2-hydroxyphenyl)ethanone (1.70g, 0.01 mmole) to an ethanolic solution of 2-chloropyridine-3-carboxamide (1.56 g, 0.01 mmole). The obtained mixture was refluxed for three hours and then allowed to cool at ambient temperature, filtered and recrystallized from ethanol. The product was dried under vacuum to get light yellow precipitate. Yield 81.32 %, m.pt. 166 °C.



Synthesis of metal complexes

All the metal complexes were prepared in a similar way by following method. To a hot solution of ligand [CHPECPC] (0.02M) in 25ml of ethanol with a suspension of respective metal salts [acetates of Cr(III), Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II)] was added drop wise with constant stirring. The precipitated complexes were recrystallized twice with ethanol, finally washed with petroleum ether (60– 80 °C), and dried under reduced pressure over anhydrous CaCl₂ in a desiccator. Yield: 45-50%.

IV. RESULTS AND DISCUSSION

All the complexes are colored solids, air stable and insoluble in water and common organic solvents but found soluble in DMF and DMSO. The analytical data indicates 1:1 metal to ligand stoichiometry for all the complexes [Table 1].

Table 1: Analytical Data, Color and Synthetic Conditions of Complexes of CHPECPC

S.N.	Compound	Color	Time of Reflux (hrs.)	Elemental analyses % found (calcd.)				
				M	C	H	N	Cl
1.	[Cr(CHPECPC)(H ₂ O) ₃].H ₂ O	Ocean spray	5.5	12.21 (12.04)	40.11 (38.91)	3.74 (3.96)	6.59 (6.48)	16.62 (16.41)
2.	[Mn(CHPECPC)(H ₂ O) ₃].2H ₂ O	Passion yellow	4	12.34 (12.12)	37.32 (37.11)	4.52 (4.23)	6.00 (6.18)	15.42 (15.65)
3.	[Co(CHPECPC)(H ₂ O)]	Dark Bayer cream	3.5	15.45 (15.30)	43.89 (43.67)	3.04 (2.88)	7.50 (7.28)	18.58 (18.41)
4.	[Ni(CHPECPC)(H ₂ O) ₃]	Bayer cream	4	13.82 (13.95)	40.21 (39.95)	3.28 (3.59)	6.42 (6.66)	17.00 (16.85)
5.	[Cu(CHPECPC)(H ₂ O) ₃]	Auckland brown	6	14.62 (14.93)	39.72 (39.50)	3.38 (3.55)	6.35 (6.58)	16.87 (16.65)
6.	[Zn(CHPECPC)(H ₂ O)].H ₂ O	Fawn Beige	5	15.78 (15.97)	41.20 (41.06)	3.41 (3.20)	7.00 (6.84)	17.15 (17.31)
7.	[Cd(CHPECPC)(H ₂ O)]	Royal Ivory	5	25.30 (25.63)	38.58 (38.34)	2.64 (2.53)	6.21 (6.38)	16.02 (16.17)

V. SPECTRAL STUDIES

¹H NMR (300 MHz, CdCl₃, δ in ppm)

The ¹H NMR spectrum of ligand was recorded in CDCl₃ at 300 MHz on a Bruker DRX-300 NMR spectrometer with TMS as an internal reference. The chemical shift values obtained as follows:

11.56 (1H, s, phenolic -OH), 8.76-8.16 (3H, m, pyridine protons), 7.91-7.15 (3H, m, Ar-H), 1.73 (3H, s, -CH₃).

IR (KBr, cm⁻¹)

IR spectra of ligand and metal complexes shows ν(C=N) peaks at 1674 cm⁻¹ and absence of C=O peak at around 1700-1800 cm⁻¹ indicates Schiff base formation. The ligand shows an intense band at 3299 cm⁻¹ indicating the presence of phenolic -OH group [12]. 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. 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 band at 1292 cm⁻¹ is due to phenolic C-O stretching. 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] [Table 2].

Table 2: Infrared Spectral Data (cm⁻¹) of CHPECPC and its Metal Complexes.

S.N.	Compound	$\nu(\text{O-H})/$ $\nu(\text{OH-N})$	$\nu(\text{C=O})$ amide	$\nu(\text{C-O})$	$\nu(\text{C=N})$	$\nu(\text{M-O})$	$\nu(\text{M-N})$	$\nu(\text{H}_2\text{O})$
1.	CHPECPC	3360	1683	1281	1630	--		--
2.	[Cr(CHPECPC)(H ₂ O) ₃].H ₂ O	--	1673	1325	1598	518	440	3427, 1544, 756
3.	[Mn(CHPECPC)(H ₂ O) ₃].2H ₂ O	--	1680	1300	1617	506	417	3404, 1516, 753
4.	[Co(CHPECPC)(H ₂ O)]	--	1682	1379	1595	514	430	3439, 1524, 817
5.	[Ni(CHPECPC)(H ₂ O) ₃]	--	1678	1381	1597	516	465	3425, 1514, 812
6.	[Cu(CHPECPC)(H ₂ O) ₃]	--	1685	1350	1599	514	426	3387, 1530, 830
7.	[Zn(CHPECPC)(H ₂ O)].H ₂ O	--	1690	1325	1597	512	430	3218, 1522,8 42
8.	[Cd(CHPECPC)(H ₂ O)]	--	1680	1323	1592	510	440	3308, 1526, 818

The synthesized complexes are colored, stable and non hygroscopic solids and are insoluble in water, ethanol and methanol but soluble in DMF and DMSO. All the complexes are found to be non-electrolytes [8-9].

VI. ELECTRICAL CONDUCTIVITY STUDIES

The electrical conductivity and activation energy values are given in the Table3. The general behavior of electrical conductivity obeys the relation, $\sigma = \sigma_0 \exp(-E_a/kT)$, Where σ_0 is a constant, E_a is the activation energy of conduction process, T is the absolute temperature and k is the Boltzmann constant. The values of electrical conductivity (σ) lie in the range of typical semiconductor [11]. The logarithm of the conductivity was plotted against reciprocal of the absolute temperature. All the plots show greater slop in high temperature region while

lower activation energy has been observed in lower temperature region. The lower temperature range is the region of extrinsic semiconductors where the conduction is due to the excitation of carrier from donor localized level to the conduction band. At the upper temperature range, the intrinsic region is reached where carriers are thermally activated from the valence band to conduction band [12]. This behavior can be attributed to interaction between the electrons of d-orbitals of metal and π -orbitals of ligand at upper temperature range. This interaction will lead to localized action of π -electronic charge on the ligand which leads to increase the activation energy. On the other hand it is known that increasing of complex stability results in decreasing conductivity due to a decrease in π -electron mobility [13] which agree with obtained results. The results of electrical conductivity are incorporated in the **Table 3**.

Table 3: Electrical Conductivity at 373 K & Activation Energy of the Complexes of CHPECPC

S.N.	Compound	Color	Electrical conductivity $\Omega^{-1} \text{ cm}^{-1}$ at 373K	Activation energy in eV
1.	[Cr(CHPECPC)(H ₂ O) ₃].H ₂ O	Ocean spray	4.57×10^{-6}	0.724
2.	[Mn(CHPECPC)(H ₂ O) ₃].2H ₂ O	Passion yellow	2.45×10^{-6}	0.524
3.	[Co(CHPECPC)(H ₂ O)]	Dark Bayer cream	2.30×10^{-6}	0.849
4.	[Ni(CHPECPC)(H ₂ O) ₃]	Bayer cream	2.40×10^{-6}	1.430
5.	[Cu(CHPECPC)(H ₂ O) ₃]	Auckland brown	3.75×10^{-6}	0.709
6.	[Zn(CHPECPC)(H ₂ O)].H ₂ O	Fawn Beige	9.19×10^{-6}	0.919
7.	[Cd(CHPECPC)(H ₂ O)]	Royal Ivory	3.78×10^{-6}	1.427

VII. CONCLUSION

The plots of $\log \sigma$ vs. $1/T$ are found to be linear over measured temperature range (313-423 K). Electrical conductivity of these complexes in the range 2.40×10^{-6} to $9.19 \times 10^{-6} \Omega^{-1} \text{ cm}^{-1}$ at 373K and is found to decrease in the order,

Zn(II) > Cr(III) > Cd(II) > Cu(II) > Mn(II) > Ni(II) > Co(II).

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