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Synthesis, characterization and electrochemical studies of symmetrical schiff base complexes of [1-(5 chloro-2-hydroxy-4-methyl phenyl) ethanone-4-chloro (-3-trifluoro methyl) aniline]

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Abstract

Schiff base complexes of Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) synthesized from 1-(2-hydroxy-5-methyl-3-nitro phenyl) ethanone and 4-chloro (-3-trifluoro methyl) aniline. The ligand and its metal complexes was characterized by elemental analysis, IR, diffuse reflectance spectroscopy. Electrochemical behaviour of these complexes has been studied by cyclic voltammetry. The cyclic voltammograms of the Mn(II)/Co(II)/Cu(II) complexes investigated in DMSO solution exhibit metal centered electro activity in the potential range -1.02 to +0.7V. Electrochemical studies of the complexes reveal that all mononuclear complexes show a one-electron quasi-reversible reduction wave in the cathodic region. The spectral data showed that the ligand behaved as a monobasic bidentate in complexes and was bonded to the metal ions *via* oxygen atom the azomethine nitrogen atom and the deprotonated phenolic hydroxyl oxygen.

Keywords: Schiff base, infrared, cyclic voltammetry etc.

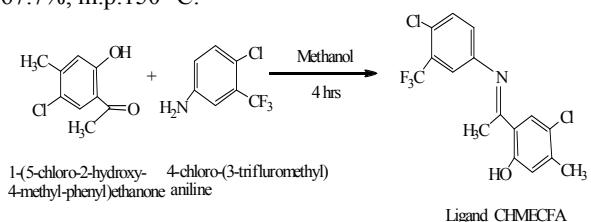
Introduction

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^[1]. The coordination sites of ligands depend on the bonding ability of it, nature of atoms, their electronegativity and steric factor. The lone pair of electrons in either π 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”^[2].

2. Materials and methods

2.1 Preparation of [1-(5-chloro-2-hydroxy-4-methyl phenyl) ethanone-4-chloro(-3-trifluoro methyl) aniline] (CHMECFA).

The Schiff base was synthesized by adding a methanolic solution of 1-(5-chloro-2-hydroxy-4-methylphenyl)ethanone (CHME) (1.84gm, 0.01M) to a methanolic solution of 4-chloro(-3-trifluoromethyl) aniline (CFA) (1.95ml, 0.01M) with 1 ml of acetic acid. The obtained mixture was refluxed for four 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 67.7%, m.p.150 °C.



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

The ¹HNMR spectrum of ligand CHMECFA indicated that different non-equivalent proton resonates at different values of applied field [3-6]. The δ-values in ppm are given below δ 8.24 (1H, s, -OH), 7.69 (1H, s, Ar-H), 7.46 (1H, s, Ar-H), 7.26-6.94 (3H, m, Ar-H), 2.61 (3H, s, -CH₃), 2.12 (3H, s, -CH₃).

2.2 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. The newly prepared ligand and its metal complexes were characterized by elemental analysis, IR and ¹HNMR spectral studies. The elemental analysis for carbon, hydrogen, nitrogen and chlorine is given in Table 1.

Table 1: Analytical Data, Color and Synthetic Condition of Complexes of CHMECFA

S.N.	Compound	Color	Solvent	Time (h)	Elemental analysis % found (calcd.)				
					M	C	H	N	Cl
1.	CHMECFA	Pale yellow	Ethanol	4		53.03 (52.89)	3.31 (3.15)	7.73 (7.55)	39.22 (39.19)
2.	[Mn(CHMECFA) ₂ (H ₂ O) ₂]	Off brown	DMF+ Ethanol	4	7.56 (7.07)	49.67 (49.42)	2.90 (2.83)	7.85 (7.20)	18.35 (18.01)
3.	[Co(CHMECFA) ₂] ² H ₂ O	Pink	Ethanol	5	7.89 (7.55)	49.85 (49.16)	2.87 (2.81)	7.35 (7.17)	18.09 (17.92)
4.	[Ni(CHMECFA) ₂ (H ₂ O) ₂] ² H ₂ O	Light green	Ethanol	4	8.53 (8.31)	49.67 (49.29)	2.96 (2.82)	7.25 (7.18)	18.18 (17.97)
5.	[Cu(CHMECFA) ₂] ²	Pale yellow	DMF+ Ethanol	4	8.51 (8.14)	49.09 (48.85)	2.98 (2.79)	7.39 (7.12)	17.98 (17.81)
6.	[Zn(CHMECFA) ₂] ² H ₂ O	Fawn Beige	Ethanol	6	8.45 (8.28)	49.26 (48.91)	2.89 (2.80)	7.67 (7.13)	18.14 (17.83)
7.	[Cd(CHMECFA) ₂] ²	Royal Ivory	Ethanol	5	13.85 (13.42)	46.21 (45.98)	2.78 (2.63)	6.89 (6.71)	16.81 (16.78)

3. 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 IR spectrum of CHMECFA and its metal complexes are found to be comparable with each other. In the IR spectrum of ligand CHMECFA, the absorption peak assigned to azomethine (-CH = N-) as a functional group is appeared at 1654 cm⁻¹. This is uncoordinated stretching vibrations occurs as coupled bands are shifted to 1637-1610 cm⁻¹ on coordination to the metal ions, indicative of the involvement of N and O donor atoms of C = N and enol groups respectively [7, 8].

The IR spectra Schiff base ligand showed characteristic broad band at 3219 cm⁻¹ ν (-OH) [9, 10]. On complexation this band disappear indicating deprotonation of the phenolic -OH by metal ion. The medium band observed at 1224 cm⁻¹ in the ligand is indicating to -C - O stretching vibration and on chelation this shows marked shift showing the metal oxygen bonding. The band at 1654 cm⁻¹ in the ligand may assigned to ν (C = N) stretching vibration of the azomethine

group which already shifted to lower frequencies in most of the complexes suggesting that this group is involved in the coordination with metal [11]. The hydrated complexes exhibited on IR band approximately by 3420-3320 cm⁻¹ in range due ν (H₂O) suggesting the coordination of water molecules in some complexes. The Mn(II) and Ni(II) complexes exhibit medium sharp bands in the range 1508-1506 cm⁻¹ and 790-804 cm⁻¹ (coordinated water) suggesting six coordinated structure [12], which is further confirmed by TGA analysis. Thus it may be concluded that Schiff base CHMECFA acts as a dibasic tetradentate ligand. In addition, the appearance of some new bands showing the involvement of M - N and M - O band in the complex formation. The Schiff base with metal ion was shown by the appearance of low frequency new bands during 578-519 cm⁻¹ range due to metal oxygen ν (M - O) stretching vibration [13, 14] confirming the involvement of oxygen and metal band in the coordination. Further formation of coordination bonding between metal and azomethine nitrogen is confirmed by new bands in the range of 459 - 426 cm⁻¹ due to ν (M - N) stretching vibrations [15].

S. N.	Compound	ν(O-H)	ν(C=N)	ν(C-O)	ν(M-O)	ν(M-N)	ν(H ₂ O)
1.	CHMECFA	3219	1654	1224	---	---	---
2.	[Mn(CHMECFA) ₂ (H ₂ O) ₂]	---	1637	1351	521	459	3320, 1508, 790
3.	[Co(CHMECFA) ₂] ² H ₂ O	---	1610	1332	519	426	3390
4.	[Ni(CHMECFA) ₂ (H ₂ O) ₂] ² H ₂ O	---	1537	1369	521	448	3420, 1506, 804
5.	[Cu(CHMECFA) ₂] ²	---	1629	1367	523	468	---
6.	[Zn(CHMECFA) ₂] ² H ₂ O	---	1629	1369	569	463	3441
7.	[Cd(CHMECFA) ₂] ²	---	1628	1369	578	480	---

3.1 Cyclic Voltammetry

The literature data observed with a diversity of redox potential for Mn(II) → Mn(III) and Mn(III) → Mn(IV)

couple. For example the value reported by Chandra *et al* [16] and for manganese complex with salen type ligand vary between - 0.3 and - 0.8 V for Mn(III) → Mn(IV) couple and

also those for Mn(III) → Mn(IV) couple range between 0.01 and + 0.6 V Vs SEC. Nevas *et al* [17] reported the values of + 0.20 and + 0.57 V vs SEC for Mn (II) → Mn (III) and Mn (III) → Mn(IV) couples respectively.

From the above literature value the waves at 0.115 V and 0.079 V Vs Ag/AgCl for manganese complex of CHMECFA can be assigned to the oxidation of Mn(II) to Mn(III), and reduction of Mn(II) to Mn(I). At second redox potential region the reduction potential wave $E_{pc} = -0.61$ V is associated with oxidation potential wave $E_{pa} = -0.502$ V and having peak to peak separation(ΔE) near about 0.108 V which suggest that reversible one electron transfer process, which is ligand based reversible process.

In case of Co(II)-CHMECFA complex the first reduction peak was observed at about $E_{pc} = 0.181$ V is associated with oxidation peak was observed at about $E_{pa} = 0.328$ V. This is quasi-reversible to cathodic peak currents (i_{pa}/i_{pc}), corresponding to the simple one electron process Co(II) → Co(I).

The second quasi-reversible process at second reduction peak was observed at about $E_{pc} = -1.348$ V gives Co(II) → Co(I) are corresponding second oxidation peak was observed at about $E_{pa} = -1.252$ V give Co (I) → Co(II) and also one electron process also [18]. The potential difference ΔE in Co complex exceeds the Nerstian requirement of 59/n mV (n = no of electron involved in oxidation – reduction). Which suggest quasi-reversible character of the electron transfer reaction [19].

The cyclic voltammogram of Cu(II)-CHMECFA complex showed new redox couple located at reduction and oxidation potential range for the first peak is $E_{pc} = 0.648$ V and $E_{pa} = 0.701$ respectively. First reduction is Cu(II) → Cu(I) and second is Cu(I) → Cu(0), from the peak current ratio it is two electron transfer redox process. Second redox potential occurs at reduction peak at $E_{pc} = -0.16$ V associated with $E_{pa} = 0.043$ V oxidation potential. The voltammetric data showed that Cu(II) was first reduced to Cu(I) and then decomposed copper metal at the cathodic region and at the anodic peak potentials was oxidized to give Cu(0) → Cu(I) and Cu(II) ions, respecting indicating that processes took place on the metal center of the complex respectively [20].

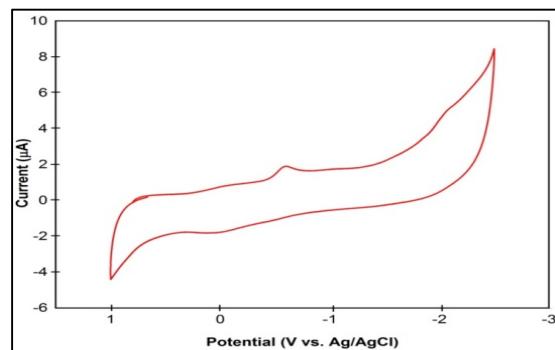


Fig 1: Cyclic Voltammogram of Mn(II) complex

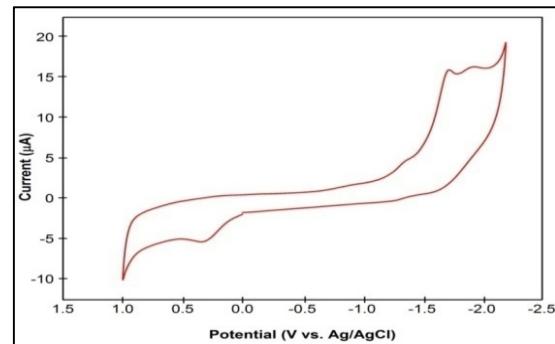


Fig 2: Cyclic Voltammogram of Co(II) complex

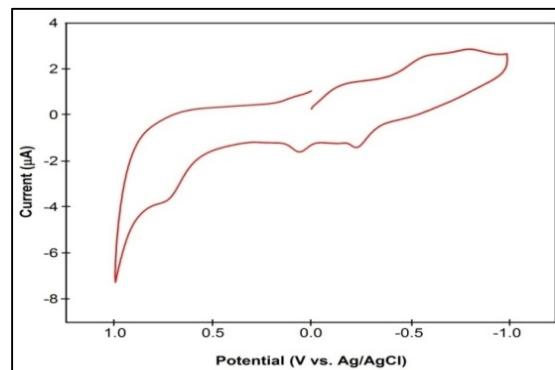


Fig 3: Cyclic Voltammogram of Cu(II) complex

Table 3: Electrochemical data of Metal complexes of CHMECFA

S. N.	Complexes	E^1_{pc} (V)	E^1_{pa} (V)	$E^1_{1/2}$ (V)	ΔE (V)	E^2_{pc} (V)	E^2_{pa} (V)	$E^2_{1/2}$ (V)	ΔE (V)
1.	Mn(II)- CHMECFA	0.079	0.115	0.097	0.036	-0.61	-0.502	-0.55	0.108
2.	Co(II)- CHMECFA	0.181	0.328	0.254	0.147	-1.348	-1.252	-1.30	0.097
3.	Cu(II)- CHMECFA	0.648	0.701	0.674	0.053	-0.16	0.043	-0.11	0.202

4. Conclusions

The cyclic voltammetry 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 voltamammogram. The values of ΔE and $E_{1/2}$ (Potential difference and half potential respectively) calculated from their respective voltamammogram. The values are obtained by plotting a graph current against potential [22].

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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