Synthesis, characterisation and thermal studies of some schiff base complexes of [1-(5-chloro-2-hydroxy-4-methyl-phenyl)ethanone]-4-(2-aminoethyl)phenol

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ABSTRACT

A Schiff base ligand derived from 4-(2-aminoethyl)phenol and 1-(-5 chloro-2- hydroxyl-4-methylphenyl)ethanone and its transition metal complexes with the metals Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) have been synthesized. The prepared Schiff base and their complexes have been structurally characterized by elemental analysis, infrared spectroscopy, magnetic susceptibility measurements and thermogravimetric study. The analytical data indicates 1:2 [M:L] stoichiometry. The thermal dehydration and decomposition of these complexes were studied kinetically using both Freeman-Carroll and Sharp-Wentworth methods. It was found that the thermal decomposition of the complexes follow first order kinetics. The thermodynamic parameters of the decomposition have also reported.

Keywords: Schiff base, IR, TGA, Kinetic and thermodynamic parameter, etc.
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INTRODUCTION

Schiff base complexes of transition metals are of particular interest to inorganic chemists because of their structural, spectral and chemical properties are often strongly dependant on the nature of the ligand structure. Coordination complexes with substituted ketones have shown diverse structural and properties generating a variety of stereochemistry and a wide range of bonding interactions. The interest in the construction of coordination complexes by reacting transition metal ions with tetradentate has been constantly growing over the past years [1-4]. Within this understanding lies an increased knowledge of molecular self-assembly [5-6], metal–ligand complexation [7-8] and disposition of metal binding sites [9]. By mastering these areas, new improved systems related to the fields of catalysis and bioengineering can be achieved and due to these applications of coordination complexes. In continuation of our earlier work, we are reporting the synthesis of Schiff base derived from 1-(5-chloro-2-hydroxy-4-methylphenyl)ethanone and 4-(2-aminoethyl)phenol. The complexes of this Schiff base with Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) have been synthesized and characterised by elemental analysis, ^{1}HNMR, IR, magnetic and thermal studies.

EXPERIMENTAL SECTION

All the chemicals were of A.R. grade and used as received. 1-(-5 chloro-2- hydroxyl-4-methylphenyl)ethanone [CHMPE]was prepared by known methods [10-13]. The solvents were purified by standard methods [14].

The ^{1}HNMRspectra of ligand was recorded in $CDCl_3$ at 300 MHz on a Bruker DRX-300 NMR spectrometer with TMS as an internal reference and elemental analysis were obtained from SAIF, CDRI, Lucknow. Infrared spectra of the ligand and its complexes were recorded in KBr pellets on FTIR-affinity-1, SHIMADZU instrument in the range 400-4000 cm^{-1}. Magnetic susceptibility was determined by Gouy's method at room temperature. Thermogravimetric analysis was performed on TGS-2, thermogravemetric analyser with TADS computer system (PERKIN ELMER) in air atmosphere at 10°C min^{-1} heating rate.

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Preparation of Schiff base ligand [CHMPEAEP]

The Schiff base was synthesised by adding a ethanolic solution of [1-(5-chloro-2-hydroxy-4 methylphenyl) ethanone] (0.1 mole) to 4-(2-aminoethyl)phenol (0.1 mole). The reaction mixture was then refluxed on a water bath for about 2 hours. The condensation product was filtered and recrystallized from ethanol. The product was dried under vacuum to get light yellow precipitate (Yield 80%). The purity of the ligand was checked by elemental analysis and TLC using silica gel.

1-(5-chloro-2 -hydroxy-4-methyl phenyl)ethanone

4-(2-aminoethyl) phenol

1-(5-chloro-2-hydroxy-4-methyl phenyl)ethanone 4-(2-aminoethyl)phenol
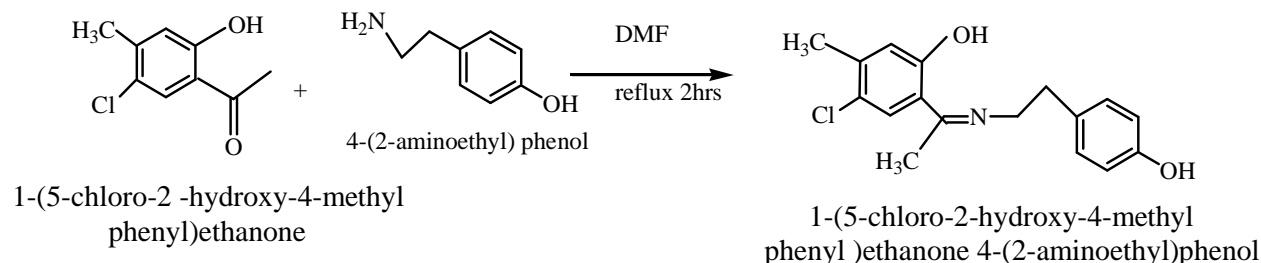
^{1}H NMR (300 MHz, CDCL$_3$ δ in ppm)

Ligand shows a multiple in the region 7.2 ppm due to phenyl ring. The singlet observed at 6.72 ppm is suggested phenolic OH group in ligand. The triplet at 3.81-3.00 ppm may be described to the proton from the CH$_2$ in the ligand. The singlet observed at 2.13 ppm is suggested the –N=C- group in the ligand.

Preparation of Metal complexes

To a ethanolic solution of Schiff base [CHMPEAEP](0.01 mole, 25 ml), a solution of respective metal acetates of [Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) ions] in ethanol (0.01 mole) was added drop wise with constant stirring. The reaction mixture was refluxed for 4-6 hours. The precipitated complexes were suction filtered, washed with ethanol and dried over fused calcium chloride. Yield**:** 50.70%, 55.80%, 70.20%, 63.22%, 59.78%, 68.32% for Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) complexes respectively.

RESULTS AND DISCUSSION

The synthesized complexes are colored, stable and non hygroscopic solids and are insoluble in water, ethanol and methanol but soluble in DMF and DMSO. The analytical data indicates 1:2 (metal: ligand) stoichiometry for all the complexes**.** All the complexes are found to be non-electrolytes [15-16]. The time of reflux, colors and constituent of elements are reported in Table 1.

Table 1: Analytical Data of CHMPEAEP and its Complexes

S. N.	Compound	Time of Reflux in hours	Colour	Elemental analysis % found (calcd).			
				M	C	H	N
1	CHMPEAEP	2	Yellow	--	76.11 (76.02)	6.71 (6.57)	5.22 (5.00)
2	[Mn(CHMPEAEP)$_2$.2H$_2$O]	4	Dark Brown	9.30 (9.15)	69.03 (69.00)	6.09 (6.00)	4.70 (4.10)
3	[Co(CHMPEAEP)$_2$].2H$_2$O	6	Pinkish Brown	9.91 (9.20)	68.91 (67.75)	5.05 (5.97)	4.70 (4.00)
4	[Ni(CHMPEAEP)$_2$.2H$_2$O]	5	Pale Green	9.61 (9.43)	68.80 (68.35)	6.07 (6.00)	4.72 (3.95)
5	[Cu(CHMPEAEP)$_2$]	4	Dark Green	10.60 (10.00)	68.00 (67.85)	6.00 (5.93)	4.66 (4.01)
6	[Zn(CHMPEAEP)$_2$]	6	Yellowish White	10.81 (10.50)	68.88 (68.02)	5.99 (5.48)	4.65 (4.00)
7	[Cd(CHMPEAEP)$_2$]	6	Opaque	17.28 (17.00)	62.96 (62.00)	5.55 (4.95)	4.32 (3.99)

IR Spectral Study

Comparison of IR spectra of Schiff base ligand with that of its metal complexes has been adopted to determine the co-ordinating atoms of the ligand to metal ions. From IR spectrum of the ligand, the absorption band at 1620 is due to the absorption of imino group –CH=N- stretching. –OH chelate stretching disappeared in ligand. The imine stretching is shifted to lower frequencies in metal complexes [17-18]. The ligand spectrum showed bands at 3300 cm^{-1} assignable may be due to hydrogen bonded phenolic –OH stretching which was absent in the spectra of the complexes. An intense ligand band at about 1259 cm^{-1} (phenolic C–O) was shifted to higher frequencies in the complexes. This suggests deprotonation of the phenolic –OH group after it's chelation with the metal ion [18-20]. The appearance of a broad band around 3320 in the spectra of the complexes suggests the presence of coordinated

water in Mn(II) and Ni(II) complexes while broad band at 3425 cm^{-1} in Co(II) may be due to lattice water in the complex. New bands of week intensity at 583-669 cm^{-1} and 418-424 cm^{-1} in the metal complexes were assigned to the ν(M-O) and ν(M-N) modes, respectively [21-23].

Thermal study and Magnetic study

The thermogravimetric analyses (TGA) of the Schiff base ligand and its chelates is used to get information about the thermal stability of these new complexes. In the present investigation, heating rates were suitably controlled at 10^{0}C min^{-1} under nitrogen atmosphere, and the weight loss was measured from the ambient temperature up to 700^{0}C. The presence of water molecule suggested from IR spectra is confirmed by TG analysis. Thermal decomposition results reveal that all the metal complexes decompose gradually. The observed weight losses of Mn(II) and Ni(II) complexes between 140-240 ^{0}C are 9.00% and 8.47% respectively could be correlated with the removal of two co-ordinated water molecules. The observed magnetic moment of Mn(II) and Ni(II) complexes found to be 5.38 and 3.21 B.M., indicating octahedral environment around central metal ion. The TG curve of Cu(II), Zn(II) and Cd(II) complexes show stable plateau upto 220 ^{0}C indicating absence of coordinated or lattice water molecule from the metal complexes. The magnetic moment value of Cu(II) complex is found to be 1.72 B.M which is well within the expected range of square planar complexes. For Co(II) complex the magnetic moment value i.e. 2.42 B.M. is lower than those expected for square planar geometry. This lowering in magnetic moment value shows subnormal character of complex due to antiferromagnetic exchange [24]. Complete decomposition of metal takes place in two steps. In the first step of decomposition in the temperature range 220-380^{0}C, indicate the decomposition of free part of ligand. In the second stage, major loss occurs between 410-600 ^{0}C, due to complete elimination of organic ligand molecule and subsequent slow oxidation. The remaining residue of the complexes at 600-710^{0}C corresponds to respective metal oxides [25].

The decomposition reaction of the anhydrous compounds (dehydration step was excluded) was subjected to non-isothermal kinetic studies. Various kinetic and thermodynamic parameters such as activation energy (E), half decomposition temperature (DH), frequency factor (Z), entropy change (ΔS) and free energy change (ΔF) were calculated from TG data as shown in the Table 3.The kinetic parameter i.e. energy of activation has been calculated by Freeman–Carroll [26] and sharp-Wentworth [27] methods. The values of kinetic parameters obtained by both methods are reasonable and quite consistent which indicate the similar types of chemical changes take place in all complexes [28]. Generally with decreasing the value of *E* the value of *Z* increase and the higher value of activation energy suggest the higher stability. Higher value of *E* (activation energy) and lower values of *Z* (frequency factor) favours the reaction to proceed slower than normal. The large negative values of entropy change and small *Z* suggest that the transition state is in highly ordered state than the individual reactants and the reactions are slower than normal [29]. Thermal stability of complexes follows the order Cd(II) > Co(II) > Zn(II) >Mn(II) > Ni(II) > Cu(II).

TABLE 2: Thermal decomposition data of CHMPEAEP and its complexes

S.N.	Compound	DH (^{0}C)	µeff. (B.M.)	E(kJmol^{-1}) F-C	E(kJmol^{-1}) S-W	Z (S^{-1})	-ΔS (JK^{-1} mol^{-1})	ΔF (kJ mol^{-1})
1.	CHMPEAEP	272	---	6.12	5.69	95.32	218.12	125.25
2.	[Mn(CHMPEAEP)$_2$.2H$_2$O]	425	5.38	18.30	16.20	221.10	238.21	217.21
3.	[Co(CHMPEAEP)$_2$].2H$_2$O	465	2.42	9.63	8.13	163.03	222.32	138.23
4.	[Ni(CHMPEAEP)$_2$.2H$_2$O]	395	3.21	6.01	4.98	160.36	332.10	115.20
5.	[Cu(CHMPEAEP)$_2$]	370	1.72	9.99	8.88	200.36	200.10	170.68
6.	[Zn(CHMPEAEP)$_2$]	450	---	10.15	9.35	195.78	242.30	142.58
7.	[Cd (CHMPEAEP)$_2$]	470	---	17.89	15.25	222.96	214.12	389.89

F-C = Freeman-Carroll, S-W = Sharp-Wentworth, DH - Half Decomposition temp.

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