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Synthesis, Characterization and Thermal Studies of Schiff Base Transition Metal Complexes derived from 1-(5-Chloro-2-Hydroxyphenyl) Ethanone

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ABSTRACT

There has been an extensive effort all over the world to develop inorganic complexes which can withstand severe conditions of temperature, oxidation and hydrolysis. While there has been no breakthrough, considerable progress has been made in this direction. Many of these complexes show thermal stability much higher than that of the organic substrate, employed as ligands in the synthesis of metal complexes. These complexes offer academic interest and at the same time provide materials of desired and superior qualities which promise a variety of applications. The Schiff base complexes have been synthesized from 1-(5-chloro-2-hydroxyphenyl) ethanone with 1, 3-diaminopropane using Mn(II), Co(II), Cr(II), Ni(II), Cu(II), Zn(II) and Cd(II) ions and characterized by elemental, spectral and thermogravimetric analysis. The ligand acts as tetradentade molecule coordinating through deprotonated phenolic oxygen atoms and azomethine nitrogen atoms. The isolated products are colored solids and are soluble in DMF and DMSO. The thermogravimetric study indicates all the complexes are stable up to $60\text{-}70^{0}$ C. All the complexes show half decomposition temperature (Table-3) and various kinetic and thermodynamics parameters have been evaluated from thermal data. The similarity in the values of kinetic parameters indicates a common decomposition reaction mode in all the complexes. The thermal activation energy of all the complexes has been calculated by Freeman-Carroll and Sharp-Wentworth methods.

Keywords: Schiff base, spectral, elemental and thermogravimetric analysis.

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INTRODUCTION

The use of Schiff base complexes as a catalyst for several organic reactions has received much attention during recent years. Schiff base are an important class of ligands in coordination chemistry and have got variety of applications in biological, clinical and analytical chemistry[1-2]. Though an extensive amount of work on a number of ONN and ONO donor ligands have resulted in the formation of metal complexes [3-6] , but no work have been done on the metal complexes of Schiff bases derived from 1-(5-chloro-2-hydroxyphenyl) ethanone and 1, 3 diaminopropane. Hence it was thought of interesting to study the reactions of this Schiff base [CHPEDAP] and its metal complexes with Mn(II), Co(II), Cr(III), Ni(II), Cu(II), Zn(II) and Cd(II) metal ions. In this communication we report, the synthesis, characterization and thermal studies of new transition metal complexes that have been obtained.

MATERIALS AND METHODS

All the chemicals were of A.R. grade and used as received. 1-(5-chloro-2-hydroxyphenyl) ethanone [CHPE] was prepared by known methods [7-10]. The solvents were purified by standard methods [11].The ^{1}H NMR spectra of ligand and elemental analysis were obtained from micro analytical 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-5000 UV-visible spectrophotometer. The thermogravimetric analysis was performed in air atmosphere at 10^0 C min^{-1} heating rate.

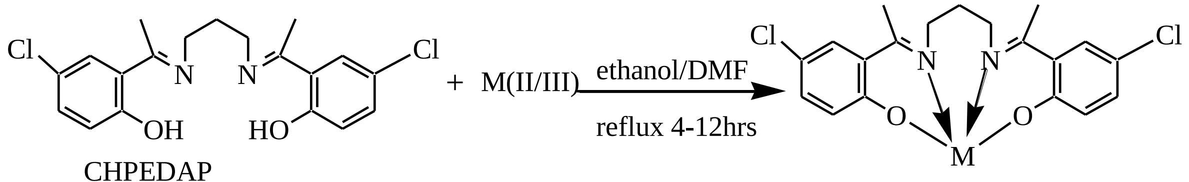
Synthesis of Schiff base ligand [CHPEDAP]:

To the solution of 1-(5-chloro-2-hydroxyphenyl) ethanone [CHPE] (25ml, 0.02M) in ethanol, 1, 3 diaminopropane [DAP] 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 ^{1}H NMR spectral studies. Yield of CHPEDAP: 61%.

Synthesis 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 with a suspension of respective metal salts [acetates of 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%.

Reaction:



CHPEDAP

Metal complex

M= Mn(II), Co(II), Cr(III), Ni(II), Cu(II), Zn(II), Cd(II)

RESULT 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 of CHPEDAP and its Complexes

S.N.	Compounds	Color	Time of Reflux (hrs.)	Elemental analyses % found (calcd.)			
				M	C	H	N
1.	HCADP	Pale Yellow	4	--	66.93 (66.99)	6.35 (6.48)	12.01 (12.11)
2.	[Mn(HCADP).2H_2O]	Cairo Bazaar	9	10.98 (11.00)	52.72 (52.90)	4.00 (4.04)	5.52 (5.61)
3.	[Co(HCADP).2H_2O]	Grayish Brown	4	11.59 (11.70)	52.46 (52.48)	3.95 (4.00)	5.41 (5.56)
4.	[Ni(HCADP).2H_2O]	Sapphire Ice	4	11.50 (11.66)	52.48 (52.51)	4.00 (4.01)	5.45 (5.57)
5.	[Cr(HCADP).2H_2O]	Graish Green	8	11.50 (11.66)	44.88 (45.44)	4.56 (4.62)	5.20 (5.33)
6.	[Cu(HCADP).2H_2O]	Raven Song	11	12.48 (12.49)	52.00 (52.01)	3.86 (3.97)	5.42 (5.51)
7.	[Zn(HCADP). 2H_2O]	Lemon Pie	10	12.70 (12.82)	51.72 (51.82)	3.80 (3.95)	5.38 (5.49)
8.	[Cd(HCADP).2H_2O]	Day Break	9	20.13 (20.18)	47.28 (47.44)	3.56 (3.62)	5.00 (5.03)

Spectral studies:

^{1}H NMR (300 MHz, $CdCl_3$, δ in ppm):

The ^{1}HNMR[12-13] spectrum of ligand was recorded in $CDCl_3$ at 300 MHz on a Bruker DRX-300 NMR spectrometer with TMS as an internal reference. δ 6.75-7.04 (6H, m, Ar-H), 1.65 (2H, s(broad) -OH), 2.34 (6H, s, $-CH_3$), 3.65-3.76 (4H, t, CH_2).

IR (KBr, cm^{-1}):

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} indicates 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)[14]. 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[15]. 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[16] (Table 2).

Table 2 : Most important IR spectral bands (cm^{-1}) of CHPEDAP and its metal complexes

S.N.	Compounds	*v*(O-H)	*v*(C-O)	*v*(C=N)	*v*(M-N)	*v*(M-O)	*v*(H_2O)
1.	HCADP	2923	1275	1612	--	--	--
2.	Mn-HCADP	--	1295	1653	470	518	3413,843,1610
3.	Co- HCADP	--	1305	1633	522	646	3440,845,1638
4.	Ni- HCADP	--	1298	1632	420	678	3428,833,1643
5.	Cr- HCADP	--	1301	1635	424	669	3435,857,1634
6.	Cu -HCADP	--	1308	1629	418	667	3428,851,1640
7.	Zn -HCADP	--	1297	1651	418	617	3419,835,1631
8.	Cd -HCADP	--	1291	1647	418	669	3438,834,1628

Thermal studies:

The study of the thermal behavior of all the complexes in air provides information about its thermal stability and nature of degradation of products produced at various temperatures. Thermal analyses of the complexes were carried out up to 700^0C. All the complexes show a gradual mass loss indicating decomposition by fragmentation with increase in temperature and follow the similar pattern of their thermal decomposition. The complexes remains unaffected up to 60^0C after this a slight depression is observed up to 120^0C. The weight loss at this temperature range is corresponds to two water molecules for Mn(II), Co(II), Ni(II), Cr(III), Cu(II), Zn(II) and Cd(II) complexes. After the loss of coordinated water, anhydrous complexes remain stable for a while at 320^0C and thereafter again the complexes show rapid degradation presumably due to decomposition of organic constituent of the molecules as indicated by the steep fall in the percentage of weight loss and continued up to 620^0C . TG curves show continuous mass loss in a temperature range 320 – 650^0C and attain a horizontal level above 650^0C suggesting the formation of final decomposition product as stable metal oxides[17-18].

The decomposition reaction of the anhydrous compounds (dehydration step was excluded) was subjected to non-isothermal kinetic studies and the kinetic parameters i.e. energy of activation, frequency factor and entropy of activation have been calculated by Freeman–Carroll and Sharp-Wentworth methods[19] and values are given in Table 3. 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 [20]. Generally with decreasing the value of *E* the value of *Z* increases 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 of activation and small *Z* suggest that the transition state is in highly ordered state than the individual reactants and the reactions are slower than normal[21]. The order of thermal stability is found to be Co > Ni > Mn > Zn > Cr > Cu > Cd (Table 3).

Table 3: Thermal decomposition data of the complexes of CHPEDAP

S.N.	**Compounds**	**DH (^{0}C)**	**Method**	**E (kJmol^{-1})**	**Z (S^{-1})**	**-ΔS (JK^{-1} mol^{-1})**
1.	[Mn(HCADP).2H_2O]	320	F-C	28.48	89.44	280.39
			S-W	26.94	159.22	279.14
2.	[Co(HCADP).2H_2O]	330	F-C	24.39	152.07	279.67
			S-W	28.22	169.44	279.53
3.	[Ni(HCADP).2H_2O]	325	F-C	20.05	319.58	272.37
			S-W	23.74	219.16	280.41
4.	[Cr(HCADP).2H_2O]	315	F-C	23.32	217.34	284.37
			S-W	27.24	189.34	274.69
5.	[Cu(HCADP).2H_2O]	310	F-C	15.13	329.05	279.13
			S-W	17.89	319.91	275.47
6.	[Zn(HCADP). 2H_2O]	320	F-C	19.60	147.50	263.26
			S-W	18.13	159.57	257.90
7.	[Cd(HCADP).2H_2O]	305	F-C	17.93	83.27	209.44
			S-W	19.39	134.35	214.27

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

CONCLUSION

In the conclusion it may be pointed out that the physicochemical methods employed in the present studies are capable giving information about nature and to some extent coordination sphere. From the above discussion we can conclude that the complexes of Mn(II), Co(II), Ni(II) and Cr(III) have an octahedral structure. The Cu(II) has distorted octahedral structure. The Zn(II) and Cd(II) complexes shows tetrahedral structure.

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