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Synthesis and thermokinetic behavior of schiff base transition metal complexes of [1-(5-chloro-2-hydroxyphenyl)ethanone-2-chloropyridine-3-carboxamide]

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ABSTRACT

The synthesis of a new Schiff base derived from 1-(5-chloro-2-hydroxyphenyl)ethanone with 2-chloropyridine-3-carboxamide and its coordination compounds with Cr(III), Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) are described. The ligand and the complexes have been characterized on the basis of analytical, electrical conductance, molecular weight, IR and electronic spectra, magnetic susceptibility measurements and thermogravimetric analysis. The ligand acts as a tribasic. The isolated products are colored solids and are soluble in DMF and DMSO. The thermogravimetric study indicates all the complexes are stable up to 60-70°C. All the complexes show half decomposition temperature 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.

Key words: CHPECPC, 2-chloropyridine-3-carboxamide, thermogravimetric analysis, metal oxides.

INTRODUCTION

Metal complexes of Schiff bases have been widely studied due to their unusual magnetic properties, novel structural features and higher thermal stability [1]. The formation of stable complexes is facilitated with the presence of functional groups, such as SH and/or OH sufficiently near to the azomethine moiety. Although there has been considerable interest in Schiff base complexes of the first transition series metal ions [2], little work has been reported on such complexes with higher valent metal ions. 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 2-chloropyridine-3-carboxamide. Hence it was thought of interesting to study the reactions of this Schiff base CHPECPC and its metal complexes with Cr(III), Mn(II), Co(II), 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

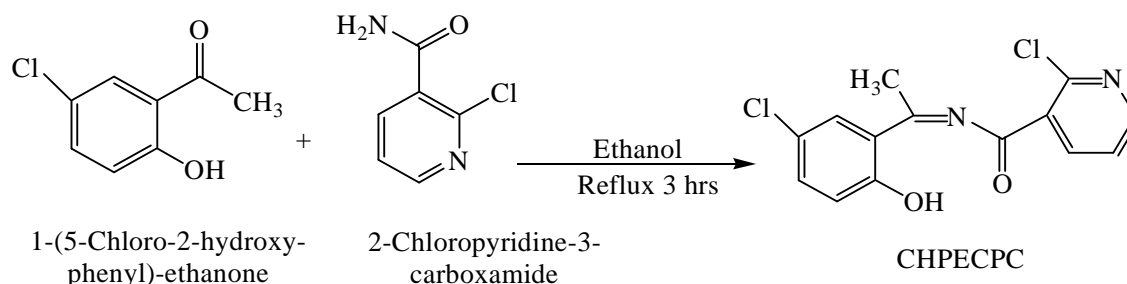
All the chemicals were of A.R. grade and used as received. 1-(5-chloro-2-hydroxyphenyl) ethanone [CHPE] was prepared by known methods [7-10]. The solvents were purified by standard methods [11].

The ¹H 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 400-4000 cm⁻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 $10^{\circ}\text{C min}^{-1}$ heating rate.

Synthesis of Schiff base ligand [CHPECPC]

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 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

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)

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

IR (KBr, cm⁻¹)

IR spectra of ligand and metal complexes show 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, 842
8.	[Cd(CHPECPC)(H ₂ O)]	--	1680	1323	1592	510	440	3308, 1526, 818

Thermal studies

Thermogram of CHPECPC and its metal complexes are shown in Fig. 1(a) and 1(b). The perusal of thermograms indicates that the complexes decomposed in a gradual manner with the exception of Cu(II) which shows slight sharp decomposition. In the present investigation, weight losses in the range 110-120°C, corresponding to two lattice water molecule [15] for Mn(II) [% wt loss: obs.(calc.): 7.42(7.94)], one lattice water molecule for Cr(III) [% wt loss: obs.(calc.): 4.35(4.16)] and one lattice water molecule for Zn(II) [% wt loss: obs.(calc.): 4.12(4.39)]. After dehydration of lattice water molecules, these complexes lose their weights [% wt loss: obs.(calc.): 11.24(11.91)], [% wt loss: obs.(calc.): 12.00(12.49)] and [% wt loss: obs.(calc.): 4.89(4.40)] respectively at around 190-210°C, corresponding to three coordinated water molecules [16] for Mn(II) and Cr(III) complexes while one coordinated water molecule for Zn(II) complex [Table 3].

The Co(II), Ni(II), Cu(II) and Cd(II) complexes shows weight loss around 185-200°C, corresponding to one coordinated water molecule for Co(II) and Cd(II) complexes and three coordinated water molecule for Ni(II) and Cu(II) complexes. Then continuous mass loss is observed upto 600 °C indicating the decomposition of free part of the complexes [17-20].

Above 600 °C TG curves attains a constant level corresponding to formation of metal oxides Cr₂O₃, Mn₃O₄, Co₃O₄, NiO, CuO, ZnO and CdO.

The relative thermal stabilities of the CHPECPC and its complexes on the basis of half decomposition temperature were deduced as Zn(II) > Cd(II) > Ni(II) > Co(II) > Cu(II) > Mn(II) > Cr(III) > CHPECPC.

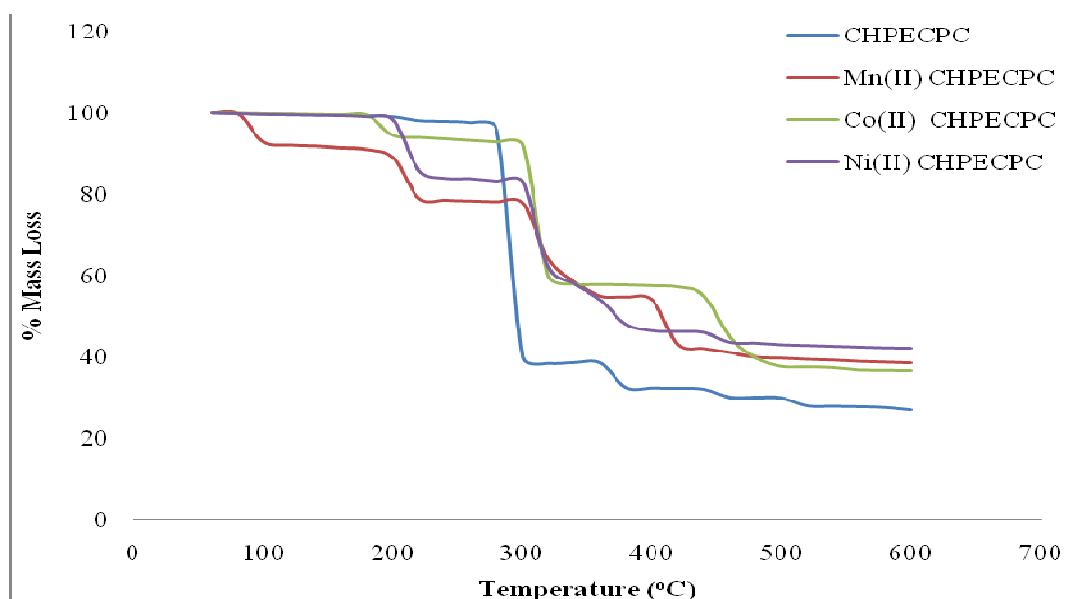


Fig. 1(a): Thermogravimetric Analysis of CHPECPC, Mn-CHPECPC, Co-CHPECPC, Ni-CHPECPC

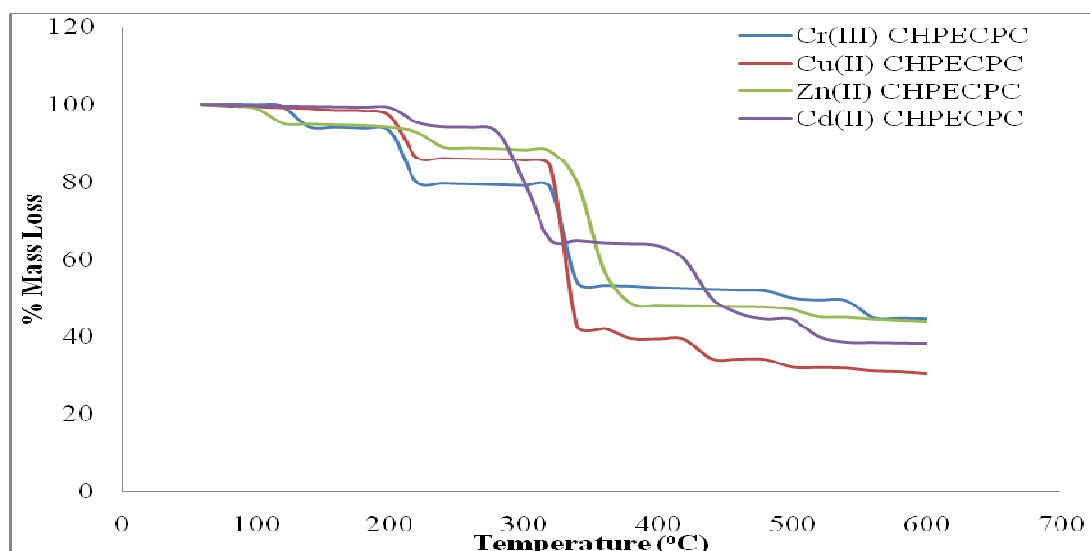


Fig. 1(b): Thermogravimetric Analysis of Cr-CHPECPC, Cu-CHPECPC, Zn-CHPECPC, Cd-CHPECPC

Table 3: Thermal and Kinetic Parameters of CHPECPC and its Complexes.

S.N.	Compound	DH (°C)	E (kJmol ⁻¹)		Z (S ⁻¹)	-ΔS (JK ⁻¹ mol ⁻¹)	ΔF (kJ mol ⁻¹)
			F-C	S-W			
1.	CHPECPC	202	36.56	34.20	110.21	245.32	125.21
2.	[Cr(CHPECPC)(H ₂ O) ₃].H ₂ O	204	31.19	35.87	140.21	280.75	125.21
3.	[Mn(CHPECPC)(H ₂ O) ₃].2H ₂ O	230	30.85	30.12	98.45	240.45	111.27
4.	[Co(CHPECPC)(H ₂ O)]	240	30.21	29.45	106.21	250.74	123.44
5.	[Ni(CHPECPC)(H ₂ O) ₃]	250	32.94	31.58	121.08	211.12	126.42
6.	[Cu(CHPECPC)(H ₂ O) ₃]	238	32.89	32.47	99.20	213.02	120.87
7.	[Zn(CHPECPC)(H ₂ O)].H ₂ O	274	37.44	29.85	130.24	220.25	118.74
8.	[Cd(CHPECPC)(H ₂ O)]	270	31.38	35.64	102.22	210.44	218.94

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.

The possible structures of CHPECPC Schiff base complexes on the basis of spectral, magnetic and thermal studies suggested octahedral geometry for Cr(III), Mn(II), Ni(II) and distorted octahedral geometry for Cu(II) while tetrahedral geometry for Co(II), Zn(II) and Cd(II) complexes.

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REFERENCES

- [1] A. Mangia, P. L. Messori, C. Pelizzi, G. Pellizi, *Inorganic Chim. Acta*, **1983**, 68, 137.
- [2] M. Kotyal, Y. Dutt, *Talanta*, **1975**, 22, 151.
- [3] A. Majundra and G. M. Rosair, *Polydron*, **2006**, 25, 1753-1762.
- [4] A. Halikedkar, R. K. Chepuri and K. M. Rao, *J. Chem. Soc. Dalton Trans*, **1997**, 10, 1697-1704.
- [5] J. T. Makode, A. R. Yaul, S. G. Bhadange and A. S. Aswar, *Russian Journal of Inorganic Chemistry*, **2009**, 54, 1372-1377.
- [6] P. V. Ananthalakshmi, J. Jayatyagaraju, M. Mikuniya, K. Nakadera, T. Tokii and P. S. Reddy, *E-journal of chemistry*, **2011**, 8, 415-420.
- [7] M. R. Maurya, *J. Chem. Sci.*, **2006**, 118, 503-511.
- [8] S. R. Kelode and P. R. Mandlik, *Int. J. Chem. Sci. and Tech.*, **2012**, 2, 231-235.
- [9] S. Pattan, M. Ali, J. Pattan, S. Purohit, V. Reddy and B. Nataraj, *Indian J. Chem.*, **2006**, 45, 1929-1932.

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- [10] S. D. Fazylov, O. A. Nurkenov and Z. S. Akhmetkarimova, *Russian J. General Chemistry*, **2012**, 82, 781-782.
- [11] H. Maradiya and V. Patel, *J. Fibers and poly.*, **2002**, 3, 314-330.
- [12] J. R. Dyer, "Application of Absorption spectroscopy Of Organic compounds", PHI learning Private limited, New Delhi, **2010**.
- [13] R. M. Silverstein and F. X. Webster, "Spectroscopic Identification of Organic Compounds", 6th ed., John Wiley and Sons, Inc, New York, **2011**.
- [14] H. S. Bhojya Naik, *Turk J. Chem.*, **2002**, 26, 565.
- [15] K. H. Reddy and M. R. Reddy, *J. Ind. Chem. Soc.*, **2002**, 79, 219-225.
- [16] M. N. Patel, S. H. Patel, M. R. Chhasatia, H. M. Parekh and P. B. Pansuriya, *J. Ther. Anal. and Calor*, **2008**, 91(2), 413-418.
- [17] M. Rahangdale, G. Pethe, A. Yaul and A. Aswar, *Res. J. Pharm. Biological and Chem. Sci.*, **2011**, 2, 341-348.
- [18] D. T. Meshram, K. P. Kariya and N. S. Bhave, *High Performance Polymers*, **2010**, 8, 1004-1016.
- [19] S. R. Kelode, *Int. J. Chem. Tech. Research*, **2012**, 4, 1442-1446, 2012.
- [20] R. B. Mohod and A. S. Aswar, *Polish J. Chem.*, **1999**, 73, 599-605.