Research Journal of Chemical Sciences ISSN 2231-606X
Vol. **7(1),** 45-48, January **(2017)** *Res. J. Chem. Sci.*

Short Communication

Synthesis and characterization of complexes of 2-chloropyridine-3-carboxamide

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Available online at: www.isca.in, www.isca.me
Received 22nd March 2016, revised 3rd December 2016, accepted 9th January 2017

Abstract

Certain metal complexes exhibit different characteristic properties depending on the nature of the metal as well as the type of ligand. 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-(2,4-dihydroxyphenyl) ethanone and 2-chloropyridine-3-carboxamide have been synthesized. The chelates have been characterized on the basis of elemental analyses, IR, ^{1}HNMR, diffuse reflectance spectral and magnetic moment studies. The complexes are found to be 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, Azomethine linkage, Diffuse reflectance, Magnetic moment.

Introduction

From more than last one decade, there has been a dramatic growth of interest in inorganic complexes based materials that exhibit unusual properties[1]. Schiff bases derived from an amine and aldehyde/ketones are an important class of ligands that coordinate to metal ion via azomethine nitrogen and have been studied extensively[2]. Schiff base complexes have been found to be important precursor for semi conducting materials[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. In the present paper, we report the synthesis and characterization of complexes derived from [1-(2,4-dihydroxyphenyl)ethanone] and 2-chloropyridine-3-carboxamide.

Materials and methods

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. The solvents were purified by standard methods. Elemental microanalysis was performed on a (C.H.N.) analyser from heraeus (Vario EL). The chloride contents for complexes were determined by using titration method on 686-Swiss potentiometer. IR spectra of the compounds were recorded on Perkin Elmer 842 spectrophotometer in the region 400-4000 cm^{-1}. ^{1}H-NMR spectrum of the ligand was recorded in DMSO-d6 on a Bruker DRX-300 FTNMR spectrometer. The diffuse reflectance spectra of the complexes were recorded on Varian Cary-5000 UV-visible spectrophotometer. The magnetic moment measurement were made on a Gouy balance at room temperature using $[HgCo(SCN)_4]$ as the calibrant.

Experimental section: Synthesis of Schiff base [DHPECPC] and its complexes: Schiff base have been synthesized by condensing the ethanolic solution of [1-(2, 4-Dihydroxy-phenyl)-ethanone] (1.52gm, 0.01mmole) to an ethanolic solution of 2-Chloropyridine-3-Carboxamide (1.56g, 0.01 mmole). The condensation product was filtered, washed with ethanol and ether, recrystalised with ethanol, and dried under reduced pressure over anhydrous $CaCl_2$. Purity of the compounds was monitored by TLC using silica gel. Schiff bases have been characterized by elemental and IR spectra.

Synthesis of Schiff base metal complexes: The Mn(II), Co(II), Ni(II), Cr(III), Cu(II), Zn(II) and Cd(II) complexes have been prepared by mixing the methanolic-ethanolic solution of corresponding metal acetates to the ethanolic solution of DHPECPC in 1 : 2 molar ratio. The precipitated complexes were recrystallized twice with ethanol, finally washed with petroleum ether (60– 80 ^oC), and dried under reduced pressure over anhydrous $CaCl_2$ in a dessicator.

Results and discussion

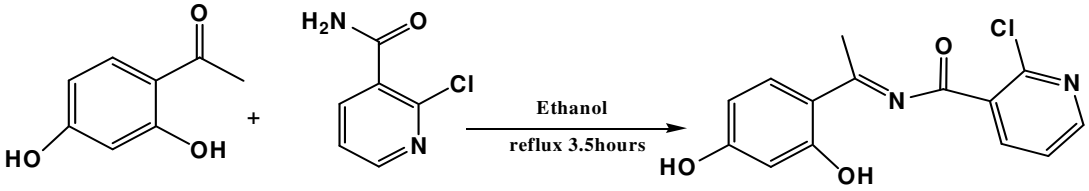
The synthesized complexes are colored, stable and non hygroscopic solids and are insoluble in water, ethanol and

methanol but soluble in DMF and DMSO. The analytical data indicate 1:2 metal to ligand stoichiometry for all the complexes**.** All the complexes are found to be non-electrolytes[7-9]. The colors, magnetic susceptibilities as well as the percentage composition of the constituent elements are reported in Table-1.

Spectral Study: ^{1}HNMR spectrum of DHPECPC (300MHz, $CDCl_3$, δ in ppm): The ^{1}HNMR spectrum of ligand DHPECPC has been recorded in $CDCl_3$. 12.69 (1H, s, phenolic –OH), 7.26-7.6 (3H, m, Ar-H), 8.21-8.78 (3H, m, pyridine protons), 6.45-5.83 (1H, s, broad, Aromatic-OH), 2.55 (3H, s, -CH_3).

IR (KBr, cm^{-1})[10]: The IR spectra of ligand and its complexes are recorded out in the range 4000-400 cm^{-1}. The IR spectra of metal complexes are interpreted by comparing with the free ligand; the results are listed in the Table-2.

Electronic Spectra: The room temperature magnetic moment values and absorption bands of Cr(III), Mn(II), Co(II), Ni(II), Cu(II) complexes is as shown in following Table-3.



1-(2,4-Dihydroxy-phenyl)-ethanone **2-Chloropyridine-3-Carboxamide** **DHPECPC**

Table-1: Analytical data, color and synthetic conditions of complexes of DHPECPC

S.N.	Compounds	Color	Solvent used	Time of Reflux (hrs.)	Elemental analyses % found (calcd.)				
					M	C	H	N	Cl
1.	DHPECPC	Leaf Brown	EtOH	3.5	--	58.00 (57.84)	3.65 (3.81)	9.85 (9.64)	12.41 (12.20)
2.	$[Cr(DHPECPC)(H_2O)_3].2H_2O$	Golden Brown	EtOH	4	12.55 (12.73)	41.94 (41.73)	5.11 (4.90)	6.31 (6.59)	8.02 (8.21)
3.	$[Mn(DHPECPC)(H_2O)_3].H_2O$	Reddish brown	EtOH	6	15.65 (15.44)	47.42 (47.20)	4.10 (3.96)	7.14 (7.35)	9.50 (9.29)
4.	$[Co(DHPECPC)(H_2O)_3]$	Golden Buff	EtOH	6	13.68 (13.48)	41.28 (41.37)	5.00 (5.86)	6.28 (6.43)	8.00 (8.14)
5.	$[Ni(DHPECPC)(H_2O)].H_2O$	Brown	DMF-EtOH	6	11.80 (11.64)	40.60 (40.32)	5.02 (5.19)	6.11 (6.27)	8.02 (7.93)
6.	$[Cu(DHPECPC)(H_2O)]$	Copper leaf	DMF-EtOH	10	16.28 (16.45)	46.37 (46.64)	4.11 (3.91)	7.10 (7.25)	9.01 (9.18)
7.	$[Zn(DHPECPC)(H_2O)]$	Brown	EtOH	7	16.70 (16.85)	46.27 (46.42)	4.01 (3.90)	7.07 (7.22)	9.00 (9.13)
8.	$[Cd(DHPECPC)(H_2O)]$	Mid Buff	EtOH	7	25.67 (25.83)	41.57 (41.40)	3.30 (3.47)	6.28 (6.44)	8.32 (8.15)

Table-2: Important IR spectral bands (cm^{-1}) of DHPECPC and its metal complexes

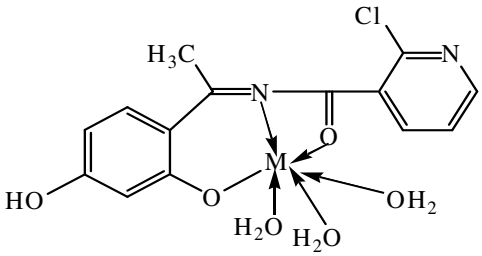
S.N.	Compound	ν(O-H)/ ν(OH--N)	ν(C=O) amide	ν(C-O)	ν(C=N)	ν(M-O)	ν(M-N)	$\nu(H_2O)$
1.	DHPECPC	3410	1674	1295	1633	--	--	--
2.	$[Cr(DHPECPC)(H_2O)_3].2H_2O$	--	1615	1317	1602	468	550	3310, 1534, 790
3.	$[Mn(DHPECPC)(H_2O)_3].H_2O$	--	1606	1316	1608	480	548	3218, 1524, 842
4.	$[Co(DHPECPC)(H_2O)_3]$	--	1602	1308	1605	461	515	3112, 1532, 820
5.	$[Ni(DHPECPC)(H_2O)].H_2O$	--	1604	1308	1615	480	516	3218, 1522, 840
6.	$[Cu(DHPECPC)(H_2O)]$	--	1625	1313	1618	479	542	3266, 1506, 803
7.	$[Zn(DHPECPC)(H_2O)]$	--	1625	1400	1596	473	540	3387, 1529, 832
8.	$[Cd(DHPECPC)(H_2O)]$	--	1610	1392	1596	482	548	3113, 1533, 827

Table-3: Magnetic Moments and Assignments of Solid State Reflectance Spectra of Complexes of DHPECPC

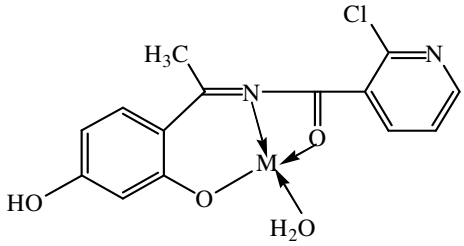
Sr. No.	Complexes	$\mu_{eff.}$ B.M.	Absorption band		Assignment
			(nm)	(cm^{-1})	
1.	$[Cr(DHPECPC)(H_2O)_3].2H_2O$	3.88	618 482 282	16181 20746 35460	$^4A_{2g}(F) \rightarrow {}^4T_{2g}(F)$ $^4A_{2g}(F) \rightarrow {}^4T_{1g}(F)$ $^4A_{2g}(F) \rightarrow {}^4T_{1g}(P)$
2.	$[Mn(DHPECPC)(H_2O)_3].H_2O$	6.12	580 420 370	17241 23809 27027	$^6A_{1g} \rightarrow {}^4T_{1g}({}^4G)$ $^6A_{1g} \rightarrow {}^4T_{2g}({}^4G)$ $^6A_{1g} \rightarrow {}^4E_g$
3.	$[Co(DHPECPC)(H_2O)_3]$	4.59	835 600 512	11905 16660 19530	$^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$
4.	$[Ni(DHPECPC)(H_2O)].H_2O$	---	728 471 398	13720 21207 25070	$^1A_{1g} \rightarrow {}^1A_{2g}$ $^1A_{1g} \rightarrow {}^1B_{2g}$ $^1A_{1g} \rightarrow {}^1E_g$
5.	$[Cu(DHPECPC)(H_2O)]$	1.82	601 524 428	16638 19083 23364	$^2B_{1g} \rightarrow {}^2A_{1g}$ $^2B_{1g} \rightarrow {}^2E_g$ C. T.

Conclusion

On the basis of physico-chemical investigations octahedral geometry is suggested for Cr(III), Mn(II), Co(II), square planer for Ni(II) and Cu(II) and tetrahedral for Zn(II) and Cd(II) as supported by infrared, magnetic and electronic spectral studies, as shown in following figures.



Where, M = Cr(III), Mn(II), Co(II)



Where M = Ni(II), Cu(II), Zn(II), Cd(II)

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