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SYNTHESIS AND CHARACTERIZATION OF FEW TRANSITION METAL COMPLEXES OF A NOVEL SCHIFF BASE LIGAND

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ABSTRACT

A novel Schiff base ligand synthesized by the condensation of 5-chloro-2-hydroxybenzophonone and 4-chloro-3-(trifluoromethyl)amine in alcohol. Cu(II), Zn(II) and Cd(II) complexes of ligand were prepared under reflux using DMF as solvent. The synthesized compounds were coloured solids and characterized by physicochemical analysis, FT-IR, ^{1}H NMR, diffuse reflectance spectra, magnetic moment measurement and TGA. Study suggests distorted octahedral geometry to Cu(II) complex and tetrahedral geometry to Zn(II) and Cd(II) complexes.

KEYWORDS: Metal Complexes, Schiff Base, Benzophenone, TGA, Diffuse Reflectance

Schiff bases metal complexes are a class of compounds in inorganic chemistry have some interesting spectral and magnetic properties and also exhibit a broad range of biological activities (Devi *et al.*, 2019; Abdel-Rahman *et al.*, 2013; Abu-Dief and Nassr, 2015). Schiff bases behave as chelating agents that can coordinated with many transition and non-transition metal ions (Osman, 2006; Ibrahim *et al.*, 2014). Some Schiff base metal complexes used as models for biological systems (Costamagna *et al.*, 1992). Many show excellent catalytic activities (Chen and Martel, 1987). Unusual properties of Schiff base metal complexes are extensively used for industrial purposes. The N, O-chelating Schiff base metal complexes have considerable stability, biological activity and many applications in different areas (Chohan and Sherazi, 1997; Bharty *et al.*, 2011; Pandeya and Sriram, 1998; Abbo *et al.*, 2005; Djebbar-Sid *et al.*, 1998). So attention has been given for their synthesis.

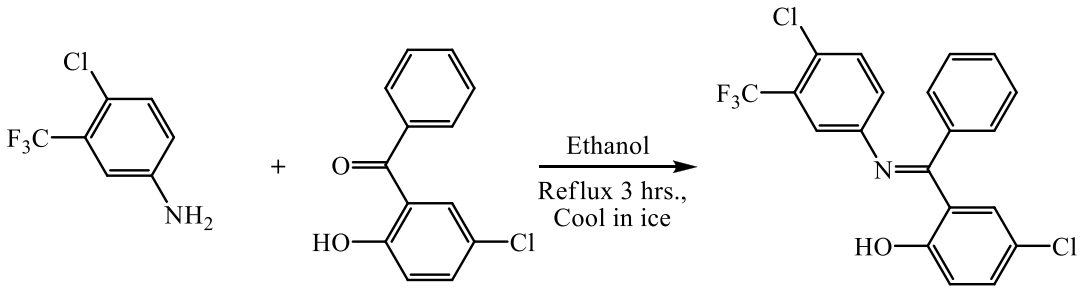
Present investigation describes synthesis and characterization of Schiff base ligand derived by the condensation of 5-chloro-2-hydroxybenzophonone with 4-chloro-3-(trifluoromethyl) amine and its Cu(II), Zn(II) and Cd(II) complexes.

EXPERIMENTAL TECHNIQUES

The metal salts of Cu(II), Zn(II) and Cd(II) used were of Merck. The organic solvents used such as ethanol, methanol, dimethyl formamide (DMF) etc. were of AR grade.

Preparation of Ligand

Schiff base ligand was synthesized by refluxing equimolar quantities 5-chloro-2-hydroxybenzophonone and 4-chloro-(3-trifluoromethyl)aniline in ethanol. The reaction mixture was then cooled in ice for one hour on a water bath.



4-chloro-3-(trifluoromethyl) aniline **5-chloro-2-hydroxy benzophenone** **(*E*)-4-chloro-2-((4-chloro-3-(trifluoromethyl) phenylimino)(phenyl)methyl)phenol**

Scheme 1: Synthesis of Schiff base ligand (SBL)

Preparation of Metal Complexes

Cu(II), Zn(II) and Cd(II) complexes were prepared by mixing solutions of Schiff base ligand and metal acetates in DMF in 2:1 molar ratio. The reaction mixtures were refluxed for 5-6 hours on a sand bath. The solid products obtained on cooling the reaction mixture were filtered and washed several times with petroleum

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ether and dried in desiccators over anhydrous calcium chloride.

RESULTS AND DISCUSSION

The synthesized complexes were coloured solids, stable in air and soluble in DMSO. Ligand was characterized by elemental analysis, ^{1}H NMR and FT-IR spectra while the metal complexes were characterized by elemental analysis, FT-IR, Magnetic studies, diffuse reflectance spectra and thermal analysis. The analytical data of ligand (SBL) and its metal complexes are given in Table 1.

Table 1: Analytical data of SBL and its metal complexes

Schiff Base/ Complex	Colour	Reflux Time (Hrs.)	Elemental Analysis % Found (Calculated)				
			M %	%C	%H	%N	%Cl
SBL	Pale Yellow	1	--	75.24 (75.11)	05.38 (05.40)	04.19 (04.17)	10.42 (10.56)
$[Cu(SBL)_2].H_2O$	Copper Leaf	6	8.53 (8.46)	67.08 (67.15)	4.92 (4.83)	3.65 (3.73)	9.59 (9.44)
$[Zn(SBL)_2].H_2O$	White	5	8.77 (8.69)	66.91 (66.99)	4.94 (4.82)	3.76 (3.72)	9.56 (9.42)
$[Cd(SBL)_2]$	Yellow	6	14.48 (14.37)	64.56 (64.50)	4.447 (4.38)	3.67 (3.58)	9.18 (9.07)

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

^{1}H NMR spectrum of SBL was recorded in $CdCl_3$ indicates different non-equivalent proton resonates at different applied field (Kidwai *et al.*, 2009; Naik and Desai, 2006; Joshi *et al.*, 2006; Campbell and Nguyen, 2001). The δ-values in ppm are shown below:

δ 7.689 (1H, s, Ar-H); δ 7.612 – 7.671 (5H, m, Ar-H); δ 7.566 (1H, s, Ar-H); δ 7.445 – 7.474 (1H, d, Ar-H); δ 7.210 – 7.260 (1H, d, Ar-H); δ 7.032 – 7.054 (1H, d, Ar-H); δ 5.453 (1H, s, (broad)-OH).

FT-IR Spectra (KBr, cm^{-1})

FT-IR spectrum of SBL was compared with its metal complexes in order to determine the coordinating atoms of ligand (Yaul *et al.*, 2009). Spectrum of SBL show strong sharp band at 1622 cm^{-1} assigned to C=N stretching which is shifted to lower frequencies by 9-46 cm^{-1} in all complexes indicating the coordination of azomethine nitrogen to the metal ion (Rizk *et al.*, 2016; Islam *et al.*, 2018). The ligand spectrum shows broad band at 3512 cm^{-1} assigned to intramolecular hydrogen bonded phenolic O-H stretching which is absent in the spectra of complexes. The characteristic medium intensity band of free ligand at 1289 cm^{-1} assigned to phenolic C-O stretching was shifted to higher frequency 6-26 cm^{-1} in the complexes further suggesting coordination through deprotonated phenolic oxygen (Rando *et al.*, 2002; Agrawal *et al.*, 2017; Al-Shemary and Fayad, 2016). The appearance of new bands in the spectra of complexes in region 579-614 cm^{-1} and 434-491 cm^{-1} assigned to the M-O and M-N stretching respectively (Bhave and Aswar, 1992; Garg and Kumar, 2003). Appearance of broad bands in the complexes in the range 3414-3423 cm^{-1} indicating hydrated complexes (Patel and Patel, 1979). The coordinated water molecules are confirmed by the bands 1584 cm^{-1} and 854 cm^{-1} assigned to H_2O (shuttle –OH rocking vibrations). The FT-IR spectral data of compounds is given in Table 2.

Magnetic Properties and Electronic Spectra

The magnetic moment value of Cu(II) complex with SBL was determined 1.92 B.M., suggesting distorted octahedral environment around Cu(II) ion (Hathway and Tomilson, 1970). In Zn(II) and Cd(II) ion, the d-orbitals are completely filled, there are no unpaired electrons. Hence, their complexes are diamagnetic in nature. Because of d^{10} configuration, the d-d transitions are not observed in Zn(II) and Cd(II) complexes.

Assignments of diffuse reflectance spectra of the metal complexes of SBL are given in Table 3 (Malik *et al.*, 2015; Raman and Thangaraja, 2005; Lewis and Walton, 1966; Warad *et al.*, 2000; Suja Pon Mini *et al.*, 2014; Parekh and Patel, 2006; Mohamed *et al.*, 2006; Montazerozohori *et al.*, 2014). The position and shape of bands in diffuse reflectance spectra of complex of Cu(II) indicates that Cu(II) ion is having a teragonally distorted octahedral environment (Aswar and Bhave, 1994; Holm *et al.*, 1971).

The three absorption bands at 14556; 17331 and 26809 cm^{-1} region can be assigned to $^2B_{1g}\rightarrow{}^2A_{1g}$, $^2B_{1g}\rightarrow{}^2E_g$ and charge transfer transitions respectively.

Table 2: FT-IR spectra of SBL and its complexes

Sr. No.	Compound	υ(O-H)	υ(C=N)	υ(C-O)	υ(M-O)	υ(M-N)	υ(H_2O)
1.	SBL	3512	1622	1289	--	--	--
2.	$[Cu(SBL)_2(H_2O)_2].H_2O$	--	1592	1295	579	475	3414, 1584, 854
3.	$[Zn(SBL)_2].H_2O$	--	1609	1302	596	491	3423
4.	$[Cd(SBL)_2]$	--	1583	1311	614	447	--

Table 3: Magnetic Moments and Assignments of Diffuse

Reflectance Spectra of metal complexes of SBL

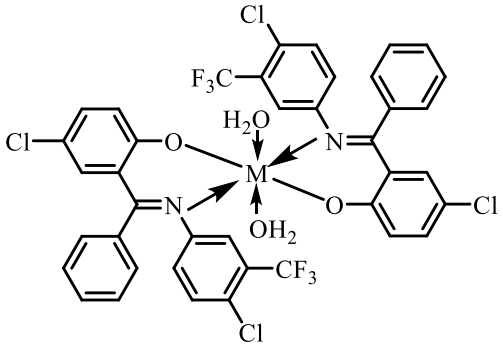
Complex	μ_{eff} B.M.	Absorption band		Assignments
		(nm)	(cm^{-1})	
$[Cu(SBL)_2].H_2O$	1.92	635	15748	$^2B_{1g} \rightarrow {}^2A_{1g}$
		558	17921	$^2B_{1g} \rightarrow {}^2E_g$
		355	28169	C. T.
$[Zn(SBL)_2].H_2O$	--	--	--	--
$[Cd(SBL)_2]$	--	--	--	--

Thermogravimetric Analysis

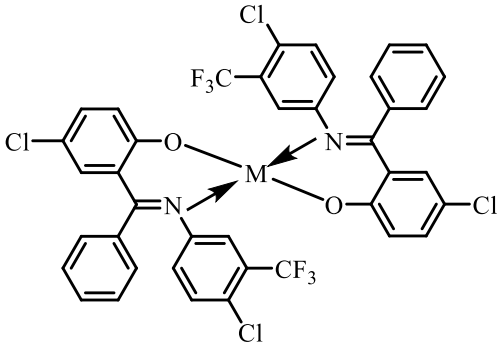
Thermogram of Cu(II) and Zn(II) complexes shows weight loss in the range 95-125°C [% wt loss: obs.(calc.): 2.17(1.92)] and [% wt loss: obs.(calc.): 2.21(1.99)] respectively, indicating presence of one lattice water molecule for each complex (Abdel-Kader and Mohamed, 2013). After loss of lattice water molecule, again, the Cu(II) complex lose its weight [% wt loss: obs.(calc.): 4.17(3.85)] around 165-190°C, indicating the presence of two coordinated water molecules (Mishra *et al.*, 2012), while Zn(II) complexes remain stable in this temperature range indicating absence of coordinated water molecules. The thermogram of Cd(II) complex show no weight loss up to ~280°C suggesting absence of lattice and coordinated water molecules.

CONCLUSION

The ligand SBL and its transition metal complexes have been synthesized and characterized by analytical, spectral, magnetic and thermal studies. The results show that SBL is a bidentate ligand and its complexes have 1:2 (Metal:Ligand) stoichiometry. The analytical and spectral studies suggest distorted octahedral geometry for Cu(II) complex, while tetrahedral geometry for Zn(II) and Cd(II) complexes.



Where, M = Cu(II)



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

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