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Research Article



SYNTHESIS OF SOME FERROCENE SCHIFF BASE COMPLEXES WITH MN (II), NI (II), CO(II), CU(II), ZN(II) AND PT(II) & ITS ANTI-MICROBIAL ACTIVITY

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Abstract

Synthesis of ferrocene Schiff bases by Condensation reaction of 5-bromo-2-hydroxy benzaldehyde with diamino ferrocene and their metal ion complexes of Mn(II), Ni(II), Co(II), Cu(II), Zn(II) and Pt(II). These synthesized complexes are characterized by elemental analysis, molar conductance, infrared, electronic spectra, magnetic moment, electronic spectra, electron spin resonance, mass spectra , thermal analysis , Scanning Electron Microscopy and EDX. The schiff base is bidentate, co-ordination through nitrogen of azomethine (>C=N-) and oxygen of Hydroxyl group. Mass spectra of the Schiff base and their complexes are agree with theoretical values, molar conductance values are very poor and all the complexes are values non –electrolytic in nature. Complexes are paramagnetic in nature except Zn (II) metal ion complex, which is diamagnetic. Electronic spectra of the complexes were recorded and its parameters like Nephelauxetic effect (), bonding parameter (b^{1/2}) and Sinha's parameter (%) are calculated. The bonding parameter reflects the participation of 3d orbital. The b^{1/2} value obtained for the present complexes indicates a decreasing order of 3d– orbital participation in the Co⁺² and Ni⁺² complexes. The average value of Sinha's parameter (%) obtained in each case is positive and smaller, indicating the presence of weak covalent bonding in the complexes. The complexes were loses two water molecules subjected to simultaneous thermo gravimetric analysis, to study their decomposition mechanism. Scanning electron Microscopy and EDX of the complexes indicate that, the size of crystal is in between 85-100 nm. These compounds were screened for in anti-bacterial and anti-fungal activity. The results of these studies revealed that, complexes exhibited significant to moderate antifungal and anti-fungal activity. The results of these studies revealed that, complexes exhibited significant to moderate antifungal and anti-bacterial properties.

Keywords: Ferrocene Schiff, Base complexes, Electronic spectra, ESR, IR, SEM, Thermal and antifungal activity

Introduction

Ferocene Schiff base compounds and its metal ion complexes are extensively investigated due to their varieties of applications in catalysts (Antony et al 2013), medicine (Chen et al, 1996), anti-corrosion agent(Shaban et al, 2013). Schiff bases are studied widely due to its 'synthetic flexibility', 'selectivity' & 'sensitivity' towards the central metal atom. The structural similarities with natural biological compounds & is due to presence of azomethine group (>CH=N-), which imports in determination of the mechanism of 'transformation' and 'racemination' reactions biologically (Lau et al ,1999). Schiff bases are allowed to form the complexes with oxygen, nitrogen, sulphur and phosphorus as a donor. Their complexes are used as

activities against bacteria, fungi, with certain type of tumors. There are many biochemical, clinical & pharmacological application of Schiff bases (Belwal et al, 2012). Azomethine groups are present in various natural, naturally occurring compounds and non-natural compounds. The imine groups present in such compounds were shown to be critical to its biological activities (Ren et al. 2002). Most of the organic reagents Schiff bases possess actually used. excellent structural similarities characteristics, with natural biological substances, relatively simple preparation procedures and the 'synthetic flexibility' that, enables design of suitable structural properties(Patai,1990 & Jungreis et al ,1989). Schiff bases are widely used in analytical determination, condensation of primary amines with carbonyl compounds in which the

drugs and reported to possess a variety of biological

azomethine bond is formed, complex formation reactions or utilizing the variation in their spectroscopic characteristics following changes in pH and solvent (Cimerman et al,2000). Unfortunately, most Schiff bases are chemically unstable and show a tendency to be involved in various equilibrium, like 'tautomeric' inter conversions, hydrolysis, or formation of ionized species (Galic et al, 1999). Therefore, successful application of Schiff bases requires a careful study of their characteristics.

Materials and Methods

5-bromosalicyldehyde with diaminoferrocene Ethanol and Methanol purchased from Aldrich and are used without any further purification. Anhydrous toluene was obtained by drying with sodium metal wire. All the glass apparatuses were dried at 120°C throughout the experimental work. The C, H and N of Ligand and complexes are determined by using micro analytical methods at IIT-Mumbai. IR spectra of the ligand and their complexes were carried out by using KBr pellets by using Perkin Elmer. Chlorides were estimated by Mohr's methods. The electronic spin resonances were recorded at RSIC-IIT, Mumbai, Electronic spectra recorded at UICT-Mumbai using DMSO and water as

ΩН

+

NH₂

 NH_2

acid/ Δ



Synthesis method of Schiff base

Microwave synthesis of new Schiff base prepared from 5-bromo-2-formylbenzoic acid (2.29g) and 1.1-(Ferrocen-2,4-dien-1-yl)-2,2'-diamine (1.59g) are dissolved separately in 50 cm³ ethyl alcohol and mixed with constant stirring on hot plate, when volume reduces to half then few drops of acetic acid is added in the reaction. This reaction mixture kept in microwave for ten minutes, the color of solution changes form deep yellow. After keeping ten minute reaction at room temperature, the product is precipitated as yellow solid and dried under vacuum and then this solid kept in decicator for long time, the yield of product is 79%.



5-bromo-2-formylbenzoic acid 1,1'-(Ferrocen-2,4-dien-1-yl)-2,2'-diamine

5-bromo-2-[(*E*)-({2'-[(4-bromo-2-carboxybenzylidene)amino]-1,1'-(Ferrocene-2,4-dien-1-yl)-2-yl}imino)methyl]benzoic acid

Synthesis method of Schiff base metal ion complexes

In the hot and magnetically stirred 50 cm³ ethanolic solution of synthesized Schiff base ligand (0.3M) 5-bromo-2-[(E)-({2'-[(4-bromo-2-

carboxybenzylidene)amino]-1,1'-(ferrocene-2,4-dien-1yl)-2-yl}imino) methyl] benzoic acid were added 0.1 M of metal chloride salts prepared in double distilled water. The reaction mixtures were stirred on hot plate for fifteen minutes and refluxed using water condenser for thirty minutes on hot water bath by adding few drops alcoholic ammonia solution. After thirty minutes reaction mixture is cooled at room temperature near about twelve hours in dark place, the coloured precipitates of metal complexes are obtained except Zn (II) complex is colorless and then these complexes filtered, washed ethanol and dried over anhydrous $CaCl_2$. All the complexes were synthesized by using similar procedure with its different metal chlorides solution.

Results and Discussion

All the prepared complexes were highly stable at room temperature and can be stored for a long period in desiccators. All the complexes were insoluble in water alcohol, benzene and so on. But they were soluble in highly polar solvent like methyl formamide & dimethyl sulfoxide. Physical and analytical data of the Schiff base and complexes are given in the table 1.

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The analytical data of the Schiff base and its complexes were in good agreement with its general formula [ML]. The complexes are paramagnetic in nature and coloured except Zn (II) metal ion complex. The study of magnetic moment & electronic spectral data is small informative in characterization the geometry of the complexes. They decomposed in the 195-230°C. melting range The point and decomposition point reported in open capillary and are uncorrected. The molar conductivity values are in agreement with electrolytic behavior of the complexes. The conductivity values of the complexes are observed in dimethyl sulfoxide in 10 $^{-3}$ molar solution. It is non-electrolytic in nature (Mishra et al, 2005). Metal contents were estimated by volumetrically by

using different indicators with ethylene diamine tetra acetic acid. Iron metals were estimated by gravimetrically and Platinum metal were estimated by AAS spectroscopic method.

Magnetic properties

The corrected magnetic moment (μ eff) in Bohr magneton units of the Schiff bases complexes are given in table 1. The magnetic moments of the complexes room temperature except that of Zinc (II) complex, which is diamagnetic and other complexes are paramagnetic in nature (Cotton et al,1962 & Figgis et al, 1976). This indicates slight participation of the 3d electron in bond formation.

Table	1. Analy	vtical d	lata and	l Physica	al Data of	Schiff	Base	and Its	Complexes	
I UDIC	1.70101	yuoui u	iala ano		i Data oi	001111	Duoc	unu no	Complexes	

Schiff base/ complexes	% yield	DP/MP°C	C%	N%	Fe%	Μ%	BM µeff
$(C_{26}H_{18}Br_2FeN_2O_4)$	79		48.94	4.39	8.75	-	-
			48.38*	4.12*	8.59*		
[Mn(C ₂₆ H ₁₆ Br ₂ FeN ₂ O ₄).2H ₂ O]	62	223-225	45.06	4.04	8.06	7.93	5.59
			44.84	3.84	7.80	7.62	
[Co(C ₂₆ H ₁₆ Br ₂ FeN ₂ O ₄).2H ₂ O]	64	214-216	44.80	4.02	8.01	8.46	4.51
			44.53	3.81	7.75	8.21	
[Ni(C ₂₆ H ₁₆ Br ₂ FeN ₂ O ₄).2H ₂ O]	58	208-210	44.82	4.02	8.01	8.42	3.24
			44.42	3.76	7.72	8.17	
[Cu(C ₂₆ H ₁₆ Br ₂ FeN ₂ O ₄).2H ₂ O]	61	201-203	44.51	3.99	7.96	9.06	1.89
			44.27	3.70	7.68	8.79	
[Zn(C ₂₆ H ₁₆ Br ₂ FeN ₂ O ₄).2H ₂ O]	55	199-201	44.39	3.98	7.94	9.30	Dimag
			44.09	3.66	7.62	9.05	
$[Pt(C_{26}H_{16}Br_2FeN_2O_4).2H_2O]$	52	195-197	37.48	3.36	6.70	23.41	-
			37.18	3.01	6.35	23.15	

Infrared Spectra

The IR spectrum provides valuable information regarding the nature of functional group attached to the metal atom. In order to study the bonding mode of Schiff bases to words metal ion complexes. Relevant IR bands that provide considerable structural evidence for the formation of ligand and complexes are reported in Table 2.The infrared spectra of complexes were compared with ligand and their substituted moieties. The IR band assignments of all metal complexes exhibit broad bands in the range of 3380 to 3510 cm⁻¹ indicating the presence of coordinated water molecules(Sarkara et al, 2008). A band at 1640 cm⁻¹ in free Schiff base is due to C = N-vibration. The shifting of this group to lower frequency (1575-1612 cm⁻¹) in the metal complexes when compared to free ligand, suggests the coordination of metal ion through nitrogen atom of azomethine group (Nakagawa et al,1964 ; Nakamoto,1970 & Shanker et al,2009). The atom of azomethine would reduce the electron density in the azomethine link and thus lower the -HC=N absorption. A band at 1680 cm⁻¹ is assigned to C=O

stretching frequency in the spectrum of free Schiff base which is also shifted to lower frequency range in1610-1640 cm⁻¹ in all the metal complexes. This indicates the involvement of oxygen atom of hydroxy group of COOH group in bonding with metal ions (Shanker et al,2009). New bands, which are not present in the spectrum of ligand, appeared in the spectra of complexes in the range of 545 - 595cm⁻¹, corresponding to M-N (Shanker et al, 2009 & Mitchell et al,1990) and 405-435 cm⁻¹ to M-O vibrations support the involvement of N and O atoms in complexion with metal ions (Soliman et al, 1999). The

C-O (Phenolic) stretching frequency of ligand is seen at 1380 cm⁻¹ and shifted to a lower frequency region in the complexes in the range of 1320-1370cm⁻¹ and this is indicate by the bonding through phenolic oxygen. Therefore, the IR spectral data indicate that the coordination sites of the metal ion are -C=N, -C-O and Ar-O. The bands observed at 3485-3510 cm⁻¹ and 3380-3435 cm⁻¹ are due to two coordinated water molecules. The central metal ions have six cocoordinated number(Padhye et al, 1985).

Schiff Base / Complexes	OH (acid)	C=N-	M-N	M-O	2H ₂ O
(C ₂₆ H ₁₈ Br ₂ FeN ₂ O ₄)	3480	1640	-	-	-
[Mn(C ₂₆ H ₁₆ Br ₂ FeN ₂ O ₄).2H ₂ O]	-	1580	595	435	3492,3385
[Co(C ₂₆ H ₁₆ Br ₂ FeN ₂ O ₄).2H ₂ O]	-	1604	572	413	3498,3428
[Ni(C ₂₆ H ₁₆ Br ₂ FeN ₂ O ₄).2H ₂ O]	-	1593	559	428	3510,3380
[Cu(C ₂₆ H ₁₆ Br ₂ FeN ₂ O ₄).2H ₂ O]	-	1575	545	405	3485,3405
[Zn(C ₂₆ H ₁₆ Br ₂ FeN ₂ O ₄).2H ₂ O]	-	1612	552	419	3490,3429
[Pt(C ₂₆ H ₁₆ Br ₂ FeN ₂ O ₄).2H ₂ O]	-	1604	573	432	3488,3435

Int. J. Curr.Res.Chem.Pharma.Sci. 2(3): (2015):89–98 Table 2. Relevant IR Spectral Data of the Schiff Base and Its Complexes in Cm⁻¹



Figure 1.(a) Infrared Spectra of (C₂₆H₁₈Br₂FeN₂O₄) Schiff Base, b): Infrared Spectra of [Zn (C₂₆H₁₆Br₂FeN₂O₄).2H₂O] complex

Mass spectra

The ESI mass spectra of the schiff base and metal complex of Cu (II) recorded at room temperature were used to compare their composition and listed in figure 2&3. The mass spectra of schiff base ligand shows a molecular ion peak at m/z = 638.51, While mass spectra of Ni (II) complex shows at m/z = 697.20 respectively, which corresponds to [M]. These peaks support to the structure of the complexes. The schiff base complex shows actual mass peak is m/z = 638.08. The different molecular ion peaks appeared in

the mass spectra of complexes (abundance range 2-100%) are attributed to the fragmentation of the metal complex molecule obtained from the rupture of different bonds inside the molecule by successive degradation leading to many more important peaks due to formation of various radicals. The spectra of complexes show molecular ion peaks in good agreement with the structure suggested by elemental analysis, spectral and magnetic studies. The spectra of the complex shows characteristic molecular ion peak at their expected m/z values confirming their monomeric forms (Karl et al ,1994 & Ingle et al,1990).





Electronic spectra

The electronic spectra of the Co (II), Ni (II) metal ion complexes have been recorded as DMF solutions in the wavelength range 380-900 nm. The spectral parameters and their assignment were listed as in table.3.The electronic d-d transition bands normally show weak perturbation due to complexation and increase in the intensity, shift to the red region and also splitting of some bands were observed on complex formation. The position shapes and of Co (II), Ni (II) were observed in solution phase using ethanol and dimethyl sulfoxide. The Co (II), Ni (II) complexes have lower energies as compared to those of aqua complex. The magnitude of the bathochromic shift of the bands in each case is meager Nephelauxetic effect (), the bonding parameter ($b^{1/2}$) and Sinha's parameter (%) have been calculated(EI-Ajaily et al, 2007; Lokhande et al, 2014 & EI-ajaily et al, 2011). The bonding parameter reflects the participation of 3d orbital. The $b^{1/2}$ value obtained for the present complexes indicates a decreasing order of 3d– orbital participation in the Co (II), Ni (II) complexes. The average value of Sinha's parameter (%) & obtained in each case is positive and smaller, indicating the presence of covalent bonding character in the complexes (Lever, 1984).

Complexes	Absorption bands cm ⁻¹	Assignments	Spectral Parameter
[Co(C ₂₆ H ₁₆ Br ₂ FeN ₂ O ₄).2H ₂ O]	22390, 16745, 11380	${}^{4}A_{2} \rightarrow {}^{4}T_{2} (F),$ ${}^{4}A_{2} \rightarrow {}^{4}A_{2} (F)$ ${}^{4}A_{2} \rightarrow {}^{4}T_{1} (P)$	= 0.9614 = 2.02 b ^{1/2} = 0.0982 = 0.01988
[Ni(C ₂₆ H ₁₆ Br ₂ FeN ₂ O ₄).2H ₂ O]	22530, 15455, 13285	³ A ₂ g (F)→ ³ T ₂ g(F) ³ A ₁ g (F)→ ² T ₂ g ³ A ₂ g(P)→ ³ T ₂ g (P)	= 0.9562 = 2.32 b ^{1/2} = 0.1046 = 0.0227

	Table	Electroni	c Spectra	of the	Complexes	and F	Parameters
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Electron Spin Resonance

The electro spin resonance spectra of copper complex provide important information in studying the structure of complex. The electro spin resonance spectra of the Cu (II) complex were recorded at room temperature (300K) and at liquid nitrogen temperature (77K). The spectrum of copper complex have a single intense absorption peak in the high field region and the molecule was isotropic due to the tumbling motion of the molecule. When the complex was frozen

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to liquid nitrogen temperature, four well resolved peaks in the low field region were obtained. This shows the presence of an octahedral geometry for the copper complex. When compared to that of room temperature in exhibiting all the hyperfine lines. The calculated values (Chandra et al, 2004 & Chandra et al, 2011) of various parameters are given in table 4.



Table 4. Electron Spins Resonance Parameters

Figure 4.(a) ESR of $[CuC_{26}H_{16}Br_2FeN_2O_4).2H_2O]$ at RT & (b) ESR of Cu (II) at 77K

Thermal analysis

Thermogravimetric and differential thermal analysis results of [Pt ($C_{26}H_{16}Br_2FeN_2O_4$).2H₂O] were reported. Complexes lose weight due to exothermic and endothermic process (Mishra et al,2000 & Shivankar et al,2003). These complexes were thermally stable at room temperature and decompose in four steps. Thermal analysis study of Pt ²⁺ complex shows loss in weight in the temperature range 20-210°C, which is corresponds to loss of two water molecule and some part of chelating agent. The experimental percentage loss, which was calculated from thermo gravimetric analysis curve, is 08.16%. This value comparable with

theoretical percentage loss. The differential thermal analysis peak at this range is endothermic. In the temperature range 220-350°C, the some part of chelating agent is lost. The major part of chelating agent is lost in the temperature range of 350-450°C. The experimental percentage loss is 31.02, which is obtained from Thermogravimatric analysis curve. The experimental percentage loss value is comparable with theoretical percentage loss value i.e. 30.60%. The probable leaving part of chelate in this temperature range is C₁₂H₄N₂ Br. The temperature range 460-1000°C leading to the formation of platinum oxide as a residue. The decomposition of complex represented as below.

Table 5: TGA/DTA Decomposition Data of the Co	omplexes	(*Exothermic Reaction)
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Complex	Temp ∘C	Calculated wt. loss %	Expt. wt loss %	Possible leaving groups
	20-220	08.16	9.10	$2H_2O, C_2H_8$
[Pt(C ₂₆ H ₁₆ Br ₂ FeN ₂ O ₄).2H ₂ O]	220-350	11.52	11.40	$C_5H_4N_2$
	350-450	30.60	31.02	$C_{12}H_4N_2Br^*$
	450-1000	52.33	53.18	PtO



Figure 5. Spectra of [Pt (C₂₆H₁₆Br₂FeN₂O₄).2H₂O] complex

Scanning Electron Microscopy and EDX of complex

SEM is a simple method can be used to check the deposited samples which clearly indicated that the nanoparticles of [Ni($C_{26}H_{16}Br_2FeN_2O_4$).2H₂O] are formed. According to the image of SEM, the diameter of the residual samples of complexes in the range 55-75 nm, shows the scanning electron microscopy picture of [Ni($C_{26}H_{16}Br_2FeN_2O_4$).2H₂O] complex.

The results by energy dispersive x-ray analysis (EDX) have indicated that there were Iron, manganese and Copper Peak and oxygen peaks, which meant there were oxygen contamination or the deposited products were Iron, nickel and nickel oxides as shown in Figure 6.

The SEM and EDX images $[Ni(C_{26}H_{16}Br_2FeN_2O_4).2H_2O]$ was shown in the Figure 6 & 7. The SEM of complex shows clearly change which were occurred on the surface of the metal ion. The shape of the particles were observed Flake type in case metal complex. Metal Particles were spherical in size quite visible throughout the complex. Further the analysis of Ni (II) metal complex shows manganese content along with N which indicates that the formation of metal complex with the schiff base compound and iron atom attached with carbon atom. SEM of the indicate that the size of the particle is near about 72 nm (Barnes et al,2002; Russell et al,1985 & Plante et al,2010).



Figure 6. SEM of [Ni($C_{26}H_{16}Br_2FeN_2O_4$).2H₂O] complex



Figure 7. EDX of [Ni(C₂₆H₁₆Br₂FeN₂O₄).2H₂O] complex

Anti-Microbial Activity

Above synthesized schiff base of ferrocene and their complexes were screened against some bacteria and fungus by the filter paper disc method at various concentrations using nutrient agar as medium. Sterilized filter paper of 5 mm diameter were soaked in solutions of different concentrations of test samples and introduced on nutrient agar plates. The schiff base and complexes were applied on a paper disc with the help of a micropipette. The discs were left in an incubator for 48 hours at 37°C and then applied on the bacteria grown agar plates. The Schiff bases ligand and its metal ion complexes shows very good activity against bacteria. The anti-microbial results of metal ion complexes are better anti-microbial agents as compared to the Schiff base ligand (Naga et al, 2013 & Prasad et al,2011). Anti-bacterial and anti-fungal

activities of the schiff base ligand and its metal complexes were screened with standard drugs like ciprofloxacin and griseofulvin. The variation in the activity of different metal complexes against different microorganisms depends on the impermeability of the cell (Nair et al,2006).

The anti-bacterial and anti-fungal results were given in table 6, shows that schiff base ligand exhibited moderate activity against all the tested bacteria and C. albicans fungus. Schiff base ligand showed high anti-fungal activity against K. fragilis and T. reesei but no activity against R. rubra. The Cu and Pt(II) complexes shows high anti-bacterial and anti-fungal activity against B. megaterium, K. fragilis and C. albicans, moderate activity against E. coli, S. aureus and P. aeruginosa, but no activity against T. reesei.

Table 6	Antibacterial	& antifundal	activity	schiff base	ligand ar	nd its metal	complexes
	Antibacteriai	a antinungai	activity		ngana ar	iu ito motai	Complexes

	E.coli	S.aureus	P.aeruginosa	B.megaterium	K.fragilis	R.rubra	C.albicans	T.reesei
Cu(II)	++	++	++	+++	+++	-	+++	-
Pt(II)	++	++	++	+++	+++	-	+++	-
ligand	+	+	+	+	+++	-	++	+++



Figure 8. Structure of the complex

Conclusion

The analytical and physical data of prepared schiff base ligand and its complexes shows the there are two coordinated molecule are attached with coordination sphere and suggested a mononuclear structure for the complexes is [M($C_{26}H_{16}Br_2FeN_2O_4$).2H₂O]. the IR spectra indicates that, boning through nitrogen of azomethine and oxygen of carboxylic acid. The electronic spectral data is in favour of octahedral geometry of the complexes. The mass spectra of the complex were comparing with theoretical value it has good agreement with its molecular weight. The complexes of Cu(II), Pt(II) and schiff base ligand were tested for anti-microbial activity against some pathogens. Both the complexes were found to be less active against the bacteria E. coli, S. aureus and P. aeruginosa, whereas the both the complexes shows the best anti-microbial activity against the bacterium B. megaterium and the fungi K. fragilis and R., rubra. The free ligand $C_{26}H_{18}Br_2FeN_2O_4$) were found to be active against the fungus T. reesei.

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