Preparation and Properties of binuclear Schiff Base Complexes of Ni(II) Cu(II)and Co(II) Inter –complex Reaction

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Abstract: Homo and hetero binuclear Schiff base complexes of NiII),Cu (II) and Co(II) were prepared by inter-complex reaction between the corresponding metal complexes of 2-hydroxy1- napthaldehyde and 2-amino 3-hydroxy pyridine. The complexes were characterized by elemental analysis and estimation of metals. Thermal behavior of the complexes was studied by TG-DTA analysis. Structures of the complexes were elucidated by spectroscopic methods like, infrared spectroscopy, UV-visible spectroscopy, mass spectrometry and ^{1}HNMR spectroscopy. The powder X-ray diffraction study suggested crystalline nature of the complexes with tetragonal geometry. Magnetic moments and electronic spectra reveal tetrahedral structure of the complexes. Antibacterial activity of complexes were studied against Gram-positive bacteria, Staphylococcus aureus, Bacillus subtilis and Gram-negative bacteria, Salmonella typhi, Escherishia coli by agar cup method. Their antifungal activity was also tested against Aspergillus niger, Penicillium chrysogenum, Fusarium moneliforme and Aspergillus flavus by poison plate method using potato dextrose agar medium at one percent concentration. All complexes show considerable antimicrobial activity.

 Keywords: biological activity.FTIR Spectra.. Thermal analysis. powder X-ray diffraction study.

INTRODUCTION

Mixed metal complexes differ from traditional complexes in the sense that they are having at least two different or same metals associated with two different ligands (metal organic ligands).the presence of more than one type of ligands in a complex increases chances of variation in properties expected for the complex .this makes the researcher interested in the synthesis of mixed metal complexes with varying properties.Synthesis and characterization of mixed metal complexes is gaining importance day by day .The increased interest in this research area has motivated

many researchers to get involved in this field. In recent years many publication are devoted to synthesis and characterization of mixed metal as well as ligands complexes.(S.V. Sanap etal 2013, L.Mrinalini etal 2014, Y.S.Malghe etal 2009, N.B.Ndosiri etal 2013, S.A.Shaker etal 2009.) The Schiff base complexes were also used as drugs and they possess a wide variety of antimicrobial activity against bacteria , fungi and it also inhibits the growth of certain type of tumors(Kovacs j. etal 2004, Kovacs j.etal2007.)The complexes formed by coordination with metal ions, have the tendency to coordinate further react with other complexes, then they may act as metal organic ligand (MOL). This MOL when allowed to react with metal ions result in the formation of mixed metal complexes. the donar atoms are unable to coordinate with the same metal ions duo to steric factors. This unutilized functionality is drawn on another metal ion forming poly nuclear complex(Greatti A. etal 2008, Oliveira E etal 2011,). Here a complex containing some unutilized functionality in ligand is considered as a ligand and named as metal organic ligand (MOL). This MOL when allowed to react with metal ions result in the formation of mixed metal complexes. We report here, a novel approach of synthesizing mixed metal complexes. It has been hypothesized that the coordinated ligands of two metal chelates can be reacted to obtain a new metal chelate. In the present work, we have allowed to react two such complexes under the conditions that permit coordinated NH_2 to react with the coordinated CHO group. Here an ionic bonds of the precursor do not dissociate and metal-ligand bonding in both the complexes

remained intact. Due to the reaction between coordinated amino and aldehyde groups, Schiff base were formed. The imine nitrogen of the Schiff base was allowed to coordinate with the metal nearby while the deficiency created at the metal ion on aldehyde end was sufficed by aquo-ligands liberated during imine formation. The resultant binuclear complex thus has one of the metal ions in diaquo form. When the metal ion in the reacting complexes was different, the resultant complex was mixed metal complex.

MATERIALS AND METHODS

2-amino 3-hydroxy pyridine and 2-hydroxy 1-napthaldehyde (>99.0%) were purchased from S D Fine Chemicals. Iron acetate, zinc acetate, manganese acetate sodium hydroxide and solvents (>99.0%) were purchased from E-Merck Ltd, Mumbai (India).The purification was done according to the needs through known procedures.

Elemental analysis (C, H, N& O) was done using Perkin Elmerseries II, 2400 CHNS/O Analyzer. The metal content of the complexes were determined by EDTA titration method in case of $Ni_2(SB)_2(H_2O)_2$.The amount of Ni(II)from homo binuclear complex $Ni_2(SB)_2(H_2O)_2$ was determined by the complex formation of Ni(II) with DMG. The precipitated of Ni-DMG was filtered ,washed and ignite in a crucible for one and half hour and then calculated gravimetrically nickel as Ni-DMG complex .The individual metal estimation of heterodinuclear complex , $NiCu(SB)_2(H_2O)_2$was done by separating the nickel from copper. Solution containing a mixture of metal ions was first treated with H_2S till the precipitated of copper sulphide is obtained and calculate as above

gravimetrically. The filtrate is used to determined nickel complex as described above..The individual metal estimation of heterodinuclear complex, $NiCo(SB)_2(H_2O)_2$ was done by separating nickel from cobalt. both the metals was estimated gravimetrical method.IR spectra were recorded on FTIR spectrophotometer model RZXC Perkin-Elmer in the range (4000-400 cm-1), ^{1}H NMR spectra were recorded on BruckerAvance II at 400 MHz using tetramethylsilane as an internal standard. Electronic spectra was recorded on Shimadzu 1800 spectrophotometer using DMSO as solvent. Mass spectra were recorded on Waters, Q-TOF Micro Mass (LC-MS). Magnetic data at room temperature were collected on Guoy balance. Mercury(II) tetrathiocynato cobalt acetate was used as a calibrant. Diamagnetic contributions were calculated for each compound by Pascal's constants. TG/DTA analysis was performed in an inert nitrogen atmosphere on Perkin Elmer STA 6000. Heating rate was 10°/min. x-ray diffractogram was scanned on Bruker AXC D.

Synthesis of Metal Complexes:

The method used in the synthesis of metal complexes consists of following three steps. In the first step, 2-amino-3-hydroxy pyridine (2A-3OH-PYR), (0.404gm) in absolute alcohol (~20mL) was prepared and a solution of nickel/copper/cobalt acetate (0.399g/0.497g) in rectified spirit (20mL),were mixed, stirred for an hour to obtain a four coordinated complex, M(2A-3OH-PYR)$_2$ in solution as shown in equation-1

$$M+2(2A\text{-}3OH\text{-}PYR) \rightarrow M(2A\text{-}3OH\text{-}PYR)_2 \quad [1]$$
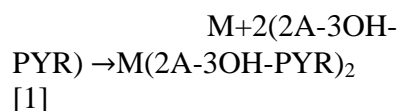
In the second step,2-hydroxy 1-napthaldehyde (2OH-1-NAPTHALDEHYDE),(0.665 g) in absolute alcohol (~20ml) was prepared and a solution of nickel/copper/cobalt acetate(0.5g, 0.1m) in rectified spirit(~20ml), were mixed and stirred for an hour to obtain a four coordinated complex, M'(2OH-1NAP)$_2$ in solution. The reaction is shown in equation 2.

$$M'+ (3E\text{-}SAL)_2 \rightarrow M' (2OH\text{-}1NAP)_2 \quad [2]$$
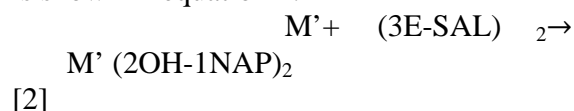
In third step, a solution of M (2A-3OH-PYR) $_2$ was added to the refluxing solution of M' (2OH-1NAP) $_2$ the reaction mixture was refluxed for 6-hours in a water bath to obtain the product under slightly alkaline condition created by sodium hydroxide. The precipitate was then filtered, washed with ethanol and dried over fused $CaCl_2$. The third step of the reaction is depicted in equation 3.

$$M(2A\text{-}3OH\text{-}PYR)_2 +M' (2OH\text{-}1NAP)_2 \rightarrow MM'(SB)_2(H_2O)_2 \quad [3]$$
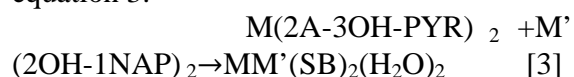
All complexes were prepared by the above discussed method .The hetero binuclear complexes, $NiCu(SB)_2(H_2O)_2$ and $NiCo(SB)_2(H_2O)_2$ were obtained by using M=Ni (II) and M'=Cu/Co (II) respectively, whereas homobinuclear complexes,$Ni_2(SB)_2(H_2O)_2$ is obtained when both M and M'=Ni (II). The melting points of all the complexes were found to be higher than 300^0 C.
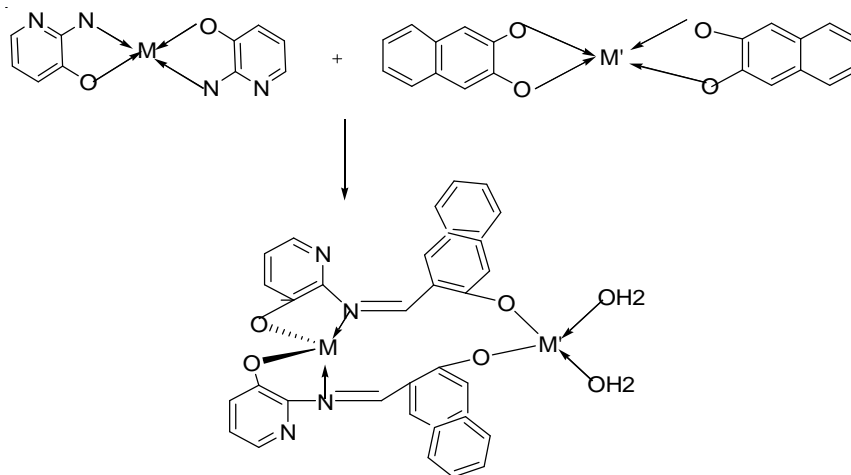
RESULTS AND DISCUSSION

The complexes are stable in air and insoluble in both polar and non polar solvents but soluble in polar coordinating solvents like acetonitrile and DMSO. Their molar conductivities are in a range that indicate non electrolytic nature of the complexes. Elemental analysis data (Table 1) obtained from experimental results was in agreement with the theoretical values within the limit of experimental error and confirmed the proposed formula of the complexes.

FTIR Spectra: The IR spectra of reactant mononuclear complexes and their binuclear complexes were compared with each other in order to investigate mode of chelation in binuclear complexes. The spectra of the precursor complex derived from 2-amino-3-hydroxy pyridine, (2A-3OH-PYR)$_2$showed a strong absorption band at 1551 cm^{-1} was assigned to coupled vibrations of NH$_2$ bending and stretching(Z. Dobrokhotova.etal 2011). Bands observed at 3322cm^{-1} and 3230cm^{-1} were attributed to NH$_2$ asymmetric and symmetric stretching frequencies respectively. A weak band at 556 cm^{-1} was observed in the complex was assigned to the M-N stretching frequency.

IR spectra of other reactant complex derived from 2-hydroxy-napthaldehyde, M'(2OH -1 NAP)$_2$ exhibited a broad and strong band at 1630 cm^{-1} was assigned to C=O stretching in the complex. A weak band at 456 cm^{-1}observed in the spectra was due to M-O stretching frequency. A band showed by both the complexes in the range3030- 3065 cm^{-1}may be due to aromatic ring vibrations. The spectra of both the reactant complexes did not show any band corresponding to the presence of coordinated water molecule .

In binuclear complex, MM'(SB)$_2$(H$_2$O)$_2$,peak due to C=O stretching (1630 cm^{-1}), NH$_2$ bending and NH$_2$ stretching (1551 cm^{-1}) was found to be absent . Emergence of a new sharp peak at 1597-1612 cm^{-1} is the evidence of imine formation.[13-14] New stronger bands appearing at 500-570 cm^{-1} and 400-480 cm^{-1} were assigned to M-O and M-N stretching frequencies. A band seen at 1203cm^{-1} may be due to C-O stretching. A sharp and strong peak between 1580-1631 cm^{-1} may be

attributed to C=N stretching was in   complex.
accordance with proposed structure of the

Table 1: FTIR spectral frequencies of complexs

Mass and ^{1}H-NMR Spectra of the Complexes:

System	ν (C=N) cm^{-1}	ν (O-H) cm^{-1}	ν(M-O) cm^{-1}	ν(M-N) cm^{-1}
M(2OH-1- NAPTHALDEHYDE)$_2$			471	
(2A-3OH-PYR)$_2$			457	551
Ni$_2$(SB)$_2$ (H$_2$O)$_2$	1631	3437	465	518
NiCu(SB)$_2$ (H$_2$O)$_2$	1620	3039	455	567
NiCo(SB)$_2$ (H$_2$O)$_2$	1587	3300	450	560

Observed mass of all the complexes are in good agreement with calculated masses of the complexes. (V.D.Bhatt etal.2012 Boca R etal.2003).

^{1}H NMR Spectra:

Spectrum of Ni$_2$(SB)$_2$(H$_2$O)$_2$in dimethyl sulfoxide,(Fig.1) showed two characteristic absorptions (singlet at δ=10.289 ppm) attributed to coordinated imine proton. Signals were observed between δ values 6 to 8 ppm attributed to six aromatic protons. The spectra showed half of the total number of hydrogen as the structure is symmetrical (C.M. Hurd etal1982).The peak observed for imine proton revealed the inter-complex Schiff base reaction.The heterodinuclear complex, NiCu(SB)$_2$(H$_2$O)$_2$, NiCo(SB)$_2$(H$_2$O)$_2$ showed similar types of spectra exhibiting the characteristic imine proton peak and the peak for 9aromatic protons between δ values 6 to 8ppm
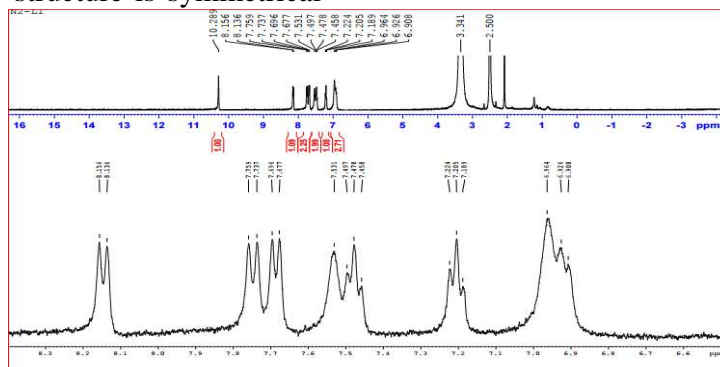

Figure 1 : Ni$_2$(SB)$_2$(H$_2$O)$_2$

Electronic Spectra and Magnetic Studies:

All the complexes showed absorption peaks in the near UVregion and these high intensity bands were due to $\pi \rightarrow \pi^*$ transitions in the aromatic group of ligand. The spectra of the homodinuclear complex The $Ni_2(SB)_2(H_2O)_2$complex in the present investigation is paramagnetic in nature. In the present investigation, electronic spectra of the complex, bands observed at 21097 (474) assigned to ^3T_1g (F)$\rightarrow ^3T_1g$ (P)and charge transfer transitions indicating tetrahedral geometry around the metal ions. In the heterodinuclear $NiCu(SB)_2(H_2O)_2$ effective magnetic moment per each ion is 3.59 B.M and $NiCo(SB)_2(H_2O)_2$complex, it was difficult to find the effective magnetic moment per each ion where as the total effective magnetic moment were high. The higher value of effective magnetic moment suggest the presence of some ferromagnetic interaction at room temperature.(M.Bocaetal 2003, G. Christouetal2007). In the present investigation complex $NiCu(SB)_2(H_2O)_2$ shows UV bands at 20,026 cm^{-1} (454)assigned to $^5T_2$ g$\rightarrow ^5$Eg and25,477 cm^{-1} (392) assigned to$^6A_1$g$\rightarrow ^4A_1$g and charge transfer transitions indicating tetrahedral geometry around the metal ions and $NiCo(SB)_2(H_2O)_2$complex shows UV bands at21,363 cm^{-1} (468), 25,188 cm^{-1} (397) assigned to $^6A_1$g$\rightarrow ^4A_1$g and charge transfer transitions indicating tetrahedral geometry of the complex

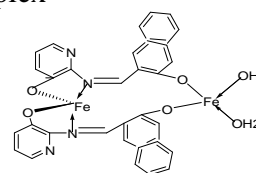**Figure 2: Proposed structure for the complex**
Table 2: Analytical Data of Metal Complexes

System	Mol. Wt g/mole	Color	% Yield	µeff per ion B.M.	Elemental Analysis % Found (Calculated)						
					%C Found (Cal)	%H Found (Cal)	%N Found(Cal)	%O Found (Cal)	%Ni Found (Cal)	%Cu Found (Cal)	%Co Found (Cal)
NiCu(SB)$_2$(H$_2$O)$_2$	675	Yellow	75	4.98	49.60 (49.66)	4.00 (4.20)	8.39 (8.40)	7.82 (7.82)	17.30 (17.37)		
NiCu(SB)$_2$(H$_2$O)$_2$	680	Green	80	*	56.43 (56.47)	2.60 (2.64)	8.20 (8.25)	14.05 (14.10)	8.650 (8.62)	9.45 (9.50)	
NiCo(SB)$_2$(H$_2$O)$_2$	676	Yellowish brown	82	5.2	39.35 (39.49)	3.40 (3.45)	7.20 (7.21)	22.22 (22.27)	8.55 (8.55)		8.70 (8.71)

Thermal analysis:

The TGA thermogram of the complexes exhibited slight weight loss below 150°C which may be attributed to the presence of small amount of adsorbed water. The weight loss in the first step above 150°Ccorresponds to the loss of two coordinated water molecules (Obs.=5.2%,Calc.=5.5% The complexes exhibited thermal stability up to 300°C after which a gradual weight loss was observed in the region 300 °C to 600°C which was attributed to ligand decomposition with mass loss(Obs.=75%, Calc.=75.50%).(P.S. Mane etal 2001, P.S. Mane etal 1961).

Powder X-ray diffraction data:

$NiCo(SB)_2(H_2O)_2$ Complex :

The $NiCo(SB)_2(H_2O)_2$ complex was used to study the X-ray powder diffraction. Diffractogram is presented in Fig. 5. The indexing in the powder diffraction was done independently by trial and error method. The crystallographic data and the indexed powder diffraction data is presented in Table 5. The standard deviation observed is within the permissible limit. The observed density for NiCo (SB) $_2(H_2O)$ $_2$ complex is 0.3333 gcm^{-3} while calculated density from Z value and unit cell volume for complex is 0.2741gcm^{-3} respectively. The porosity percentage calculated from the observed and calculated densities was found to be17.16. The crystal system was found to be monoclinic with 2 molecules per unit cell having probable space group P. The lattice parameters reported are a = 12.55611 Å b = 5.766040Å c = 10.66775Å β = 96˚ and α = γ = 90˚, characteristic of monoclinic crystal system.

Hence the X-ray powder diffractogram suggests that $NiCo(SB)_2(H_2O)_2)$ complex under investigation crystallize with monoclinic crystal system with probable space group P.

Table 3: Indexed X-ray Diffraction Data of $NiCo(SB)_2(H_2O)_2$ Complex

Peak No.	2θ (observed)	2θ (calculated)	d (observed)	d (calculated)	Miller indices of Planes			Relative intensities (%)
					h	K	L	
1	4.16599	4.15979	10.62947	10.61921	0	0	1	100
2	5.72236	5.73601	7.69903	7.70722	1	0	1	91
3	7.08695	7.07910	6.25250	6.25042	-2	0	0	70
4	8.47745	8.45352	5.23146	5.23988	1	1	0	69
5	9.59319	9.59848	4.62710	4.61969	1	1	1	59
6	10.39579	10.38822	4.27300	4.27192	-2	0	2	52
7	11.86966	11.85809	3.74821	3.74862	3	0	1	45

| 8 | 12.71761 | 12.70402 | 3.50180 | 3.50272 | -1 | 0 | 3 | 39 |

Unit cell data and crystal lattice parameters

a (A˚) =12.55611

b (A˚) =5.766040

c (A˚) =10.66775

α =90˚

β = 95.96˚

γ=90˚

Standard deviation (%) = 0.087

Volume (V) = 768.155A$^{\circ 3}$

Density (obs.) = 0.3333gcm^{-3}

Density (cal.) = 0.2741gcm^{-3}

Z =2

Crystal system= Monoclinic

Space group = P

Porosity = 17.16%
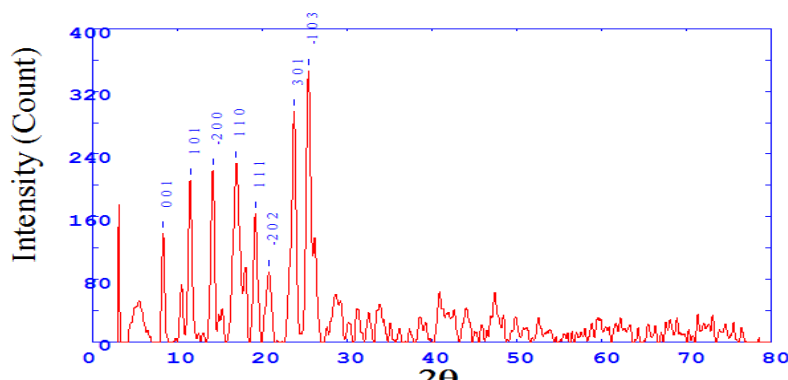
Fig:3 NiCo(SB)$_2$(H$_2$O)$_2$

Table 4: Report of antibacterial testing

Sr. No.	Test Compound	Inhibition Zone (nm)			
	Method –Agar cup method		Dose of compound -1% cup size-10mm		
		Escherishia coli	Salmonella typhi	Staphylococcus aureus	Bacillus subtilis
	Penicillin	14 mm	20 mm	36 mm	28 mm
01	Ni$_2$(SB)$_2$(H$_2$O)$_2$	15	-ve	20	16
02	NiCu(SB)$_2$(H$_2$O)$_2$	-ve	-ve	16	16
03	NiCo(SB)$_2$(H$_2$O)$_2$	-ve	-ve	-ve	-ve

Zone of inhibition:-in mm

Medium: Potato Dextrose Agar method   Method: Poison plate
Dose: 1%

Table57: Report for antifungal testing

Antimicrobial activity of the complexes:

Test compound	Inhibit			
	Aspergillus Niger	Penicillium Chrysogenum	Fusarium Moneliforme	Aspergillus flavus
Griseofrin	-ve	-ve	-ve	-ve
$Ni_2(SB)_2(H_2O)_2$	RG	RG	RG	RG
$NiCu(SB)_2(H_2O)_2$	RG	RG	-ve	RG
$NiCo(SB)_2(H_2O)_2$	RG	RG	-ve	RG

The antibacterial activity of the complexes were tested against the standard microbial strains, Escherishia coli, Salmonella typhi, Staphylococcus aureus and Bacillus subtilis by agar cup method(K.C. Mondal etal 2010).at fixed concentration of 1% and compared with known antibiotic,Penicillin (Table 4). For fungicidal activity, compounds were screened in vitro against Aspergillus Niger, penicilliumchrysogenum, Fusarium moneliforme, Aspergillusflavus by poison plate method with potato dextrose agar media. The complexes were tested at 1% concentration in DMSO and compared with control (Table 4).

The complexes individually show varying degrees of inhibiting effects on the growth of the different bacterial species. Homodinuclear complexe of Ni(II) is found to be highly active against one of the Gram –ve bacteria E coli. Their activity is higher than that of standard, Penicillin .However it was found to be inactive against other Gram –ve bacteria , S. typhi. On the other hand heterodinuclear complex $NiCu(SB)_2(H2O)_2$is active against Staphylococcus aureus, Bacillus subtilis and inactive against other Gram –ve bacteria The $NiCo(SB)_2(H_2O)_2$ is inactive against all Gram +ve and Gram –ve bactria

Conclusion:

The preparation of dinuclear complexes by a novel synthetic route is strongly supported by analytical data. The formation of precursor complexes as well as imine in dinuclear complexes confirmed by existant and missing peaks in infrared spectra. The effective magnetic moment and electronic spectral deta supported the tetrahedral environment in the metal ion.

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