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CHARACTERIZATION AND BIOLOGICAL EVALUATION OF NEWLY SYNTHESIZED BIMETALLIC COMPLEXES OF NI (II), CD(II) AND HG(II) WITH N, N,'-BIS-(BENZYLIDENE)-1,3, PHENYLENEDIAMINE SCHIFF BASE

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ABSTRACT

A new series of the bimetallic complexes of Ni(II), Cd(II) and Hg(II) of Schiff base ligand N, N', - Bis (Benzylidene)-1, 3 – Phenylenediamine (BENDAMB 1,3) have been synthesized these were characterized by elemental analysis, molar conductance, magnetic moment measurements and by IR, Electronic and ^{1}H NMR spectral studies. The softness parameter TEn$^{\neq}$ of complexes have also been calculated to derive the binding side of the thiocyanate ligand. The softness parameter suggest monomeric bridged structure for these complexes, magnetic susceptibility measurements indicate square planar geometry around Nickel ion. Newly synthesized bimetallic complexes have been evaluated for their antimicrobial and antifungal activities and was compared with solvent, screening results indicates that the metal complexes are moderately active compared to solvents.

KEYWORDS: Schiff base, Bimetallic, Softness Parameter, Antimicrobial activity.

INTRODUCTION

Transition metal complexes have been widely explored because of their catalytic property and versatile activities including antifungal and insecticidal activities[1], while Schiff Bases are good ligands.

Schiff bases are the condensation products of carbonyl compound (ketone or aldehyde) with primary amines, first invented by Hugo Schiff, which was named after him[2], these ligand are widely studied because of their coordinating properties and abilities, due to special property

of -C=N group (azomethine)[3], they are used as chelating ligand in coordination chemistry of transition metals, model system for biological macro molecules.[4-5]

The importance of Schiff base complexes for bioinorganic chemistry, biomedical applications, supra molecular chemistry has been well recognized and reviewed, they show biological activity including antibacterial, antifungal and herbicidal activity.[6-7]

Bimetallic Schiff base complexes have better biologically activity due to biocompatible metal ions in the complexes[8-9], the diversified application of the transition metal complexes of Schiff bases leads us to design Schiff base ligand and their transition metal complexes.

In this paper we have reported synthesis characterization and biological evaluation of bimetallic complex of the fallowing type.

$[MM'(SCN)_4]$ → $[(BENDAMB(1,3))M(NCS)_2M'(SCN)_4]$

\+ 1: 2: 1

[Benzaldehyde] ----------

\+

[1, 3- Phenylenediamine] → $[(BENDAMB(1,3))]^{2+}[M'(SCN)_4]$

BENDAMB (1, 3) = N,N'-bis(benzylidene)-1,3-phenylenediamine

MATERIALS AND METHODS

Solvents were dried and distilled in usual manner Nickel (II), Cadmium(II) and Mercury(II) nitrate (all BDH) were used as received without further purification. Potassium thiocyanate (Sarabhai M. Chemicals) was used after drying in vacuum. Phenylenediamine and Benzaldehyde (both CDH) were used as received.

Molar conductance were measured in acetone and DMSO with the help of Century CK-704 Conductivity bridge (Type digital portable kit) using a dipping type of cell at 298 ± 2^0K.

Gouy's method was employed for the measurement of Magnetic Susceptibility. Diamagnetic Correction were also made using Pascall's constant. The metal and sulphur content were analyzed using standard methods.[10]

FTIR spectra were measured on a Perkin-Elmer spectrometer RXI, using KBr pellets. The Electronic spectra were recorded on a Perkin-Elmer LAMBDA-15 UV/VIS spectrophotometer in acetone/DMSO. ^{1}H –NMR spectra was recorded on Burker DRX-300 in DMSO.

Preparation of Bimetallic Complexes

Bimetallic complexes of N,N'-bis(benzylidene)-1,3-phenylenediamine [BENDAMB(1,3)] Schiff base were synthesized by template method.[11] Metal dithiocyanate were prepared by fallowing literature procedure[12], both $M(SCN)_2$ and $M'(SCN)_2$ were mixed in 1:1 ratio for the preparation of bimetallic Lewis acid $MM'(SCN)_4$, the calculated amount of benzaldehyde (2 mol) was added into the solution of $MM'(SCN)_4$ and stirred for 5 minutes and then 1 mol of 1,3-phenylenediamine was added and whole reaction mixture was stirred for 6-8 hr. After constant stirring of reaction mixture, in each case a solid was separated which was filtered off and washed with methanol, dried in vacuum and recrystallized from Acetone/Chloroform.

All bimetallic complexes were partially/completely soluble in DMSO.

RESULT AND DISCUSSION

The stoichiometry of the complexes are in agreement with elemental analyses given in **Table-1** The lower value of conductance in DMSO is indicative of non-electrolytic behavior of complexes.

Table – 1: Elemental analyses, color, yield & melting point of the complexes.

S. N.	Complexes	Color	Yield	M.P.	M Ni/Cd	M' Cd/Hg	S
1	[BENDAMB(1,3)Ni$(NCS)_2$Cd$(SCN)_2$]	Green	52	173^d	8.39 (8.53)	16.20 (16.34)	18.30 (18.64)
2	[BENDAMB(1,3)Ni$(NCS)_2$Hg$(SCN)_2$]	Green	50	160^d	7.30 (7.56)	25.67 (25.85)	16.27 (16.52)
3	[BENDAMB(1,3)Hg$(NCS)_2$Hg$(SCN)_2$]	White	56	170^d	-	43.40 (43.70)	13.71 (13.97)

Satisfactory C, H, N analyses have been obtained for all complexes; **d**-decompose.

1.1. Electronic spectra and Magnetic moments

All the bimetallic Complexes are diamagnetic in nature, Electronic spectra of the complexes viz.- 1 & 2 show a band between 25160-26210cm^{-1} which can be assigned for the transition $^1A_1(g) \rightarrow {}^1B_1(g)$ (ν_2) and another band between 31010-32700cm^{-1} may be attributed for the

transition $^1A_1(g) \rightarrow {}^1B_3(g)$ (ν_3). The electronic spectra of these complexes also exhibit a charge transfer band. The homo-bimetallic complex exhibit charge transfer band only.

Electronic spectral assignments of the complexes viz. - 1 & 2 suggest Square Planar environment around Nickel ion[13] while tetrahedral environment around mercury ion.

1.2. IR spectra analyses

The infrared spectra of these complexes (presented in **Table-2**) exhibit four bands in – C-N stretching region. The presence of two bands in between 2113-2162 cm^{-1} clearly indicates the presence of thiocyanate as bridging unit. Similarly the presence of two characteristic ν(CN) bands for S-bonded terminal SCN Furthermore, the presence of bands in δ(NCS), ν(C-S), ν(M-N) and ν(M'-S) regions are diagnostic for the nature of thiocyanate bonding.[12]

All the assignments are in favor of monomeric bridge structure for these complexes. A strong band in the region 1633cm^{-1} appears in Schiff base characteristic of azomethine (>C=N) group.[14-15] This band is shifted towards the lower frequency region (~20-45cm^{-1}) in the bimetallic complexes indicative of Schiff base azomethine nitrogen atoms.

Table. 2.

S. N.	Complexes	C-N (Str)	C-S (Str)	δNCS (bend)	>C=N(Str) azomethine	ν(M-N)	ν(M'-S)	Structure
1	[BENDAMB(1,3)Ni(NCS)$_2$ Cd(SCN)$_2$]	2123(sh);2160(s) 2068(s);2084(sh)	731(m);769(s) 721(sh)	470(w) 420(m)	1594(s)	309(m)	227(w)	M.B
2	[BENDAMB(1,3)Ni(NCS)$_2$ Hg(SCN)$_2$]	2113(sh);2151(s) 2064(s);2100(m)	746(m);770(s) 728(sh)	481(w) 417(m)	1587(s)	311(m)	226(w)	M.B
3	[BENDAMB(1,3)Hg(NCS)$_2$ Hg(SCN)$_2$]	2115(sh);2162(s) 2090(sh);2102(s)	730(m);789(s) 721(sh)	504(m) 471(s) 411(m)	1610(s)	297(w)	238(w)	M.B

1.3. ^{1}H-NMR spectra

The ^{1}H-NMR spectra of the complexes recoded in DMSO given in **Table-3**.

The fallowing conclusion can be derived.

(1) The ^{1}H NMR spectrum shows a signal between δ7.10-7.70 due to aromatic ring in all complexes.

(2) A proton signal due to -CH=N group appears in between δ8.55-8.89 in the complexes due to lone pair donation to metal from nitrogen.

Therefore on the basis of Electronic spectra, IR spectra and ^{1}H NMR spectra we suggest Monomeric bridged structure for the complexes, in which SCN from bridge between two metals and Schiff base ligand is linked with comparatively harder metal like Ni^{2+}

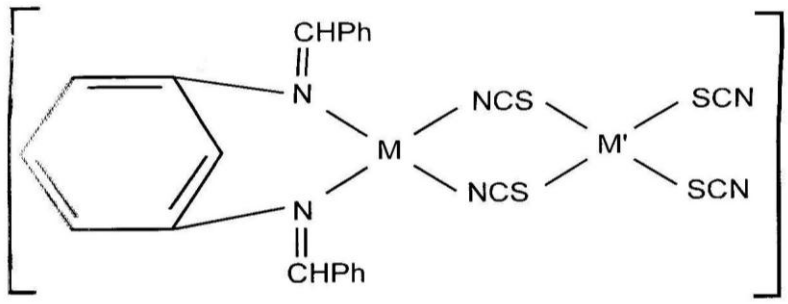
Table 3 - ^{1}H NMR data (scale ppm) of the complex

S.N	Complexes	Aromatic ring	-CH=N
1	[BENDAMB(1,3)Ni(NCS)$_2$Cd(SCN)$_2$]	7.15(s) 7.60(m)	8.55(s)
2	[BENDAMB(1,3)Ni(NCS)$_2$Hg(SCN)$_2$]	7.17(s) 7.70(m)	8.89(s)
3	[BENDAMB(1,3)Hg(NCS)$_2$Hg(SCN)$_2$]	7.10(s) 7.40(m)	8.71(s)

Mono-meric bridged structure (A) for the complexes 1, 2, 3 are also supported by the fallowing ground.

(a) The Nickel complexes are low spin, it is not surrounded by four NCS group because the $[Ni(NCS)_4]^{2-}$ ion is high spin.

(b) HSAB theory[16] also support the binding possibility of thiocyanate ion in metal complexes 1-3 sulphur end will be attached with soft Cadmium and Mercury metal ions, whereas nitrogen of thiocyanate was well linked with comparatively harder Nickel.



(A)

1.4 Application of softness parameter to the nature of bridge

Quantitative softness value of M and M' (M=Ni; M' =Cd, Hg) and thiocyanate ion are related with nature of the complexes i.e. Monomeric bridged. These softness values are derived by quantum mechanical procedure pioneered by Klopman.[17]

The total softness values of M and M' have been derived by adding the softness values of ligand to the reported values of M and M'. The obtained values of softness parameter $TEn^{\neq}$(M-M') for complexes 1, 2, 3 are in between 18.77-23.03 which can be accounted for monomeric bridged structure. The $TEn^{\neq}$ (M-M') values and predictions are presented in Table **-4.**

Table. 4.

S. N	Complexes	$TEn^{\neq}$ (M-M')	Nature of Bridge
1	$[BENDAMB(1,3)Ni(NCS)_2Cd(SCN)_2]$	19.86	M.B
2	$[BENDAMB(1,3)Ni(NCS)_2Hg(SCN)_2]$	18.77	M.B
3	$[BENDAMB(1,3)Hg(NCS)_2Hg(SCN)_2]$	23.03	M.B

Antimicrobial and Antifungal activities

(a) Antibacterial activity Complexes were screened to evaluate their antibacterial activity against bacteria **(*E.coli*, *P.aurginisa*)**. All the complexes shows superior activity compared to

solvent, which can be explained on the basis of Tweedy theory[18] The Schiff base can penetrate the bacterial cell membrane by coordination of metal ion. Screening results are tabled in. Table **5a.**

Table. 5a.

S.N	Sample	*E.coli*	*P.aurginisa*
1	DMSO	-	-
2	[(BENDAMB(1,3) $Ni(NCS)_2Cd(SCN)_2$]	++	+
3	[(BENDAMB(1,3) $Ni(NCS)_2Hg(SCN)_2$]	++	++
4	[(BENDAMB(1,3) $Hg(NCS)_2Hg(SCN)_2$]	+++	++

(-) zero activity, (+) less active, (++) moderately active, (+++) highly active.

(b) Antifungal Screening

The fungicidal activity of the complexes was evaluated against ***A.flavus*** and ***F.solani*** by Agar plate technique. At the three concentration 1000 ppm, 100 ppm and 10 ppm,

The average percentage inhibition after 96 hr by various Compound was calculated from the given expression

(%) inhibition = 10 (C-T) /C

Where C = diameter of fungus colony in control plates after 96 hr and T = diameter of fungus colony in tested plated after 96hr. The results compiled in Table -5, all the complexes show significant toxicity at 1000 ppm and 100 ppm but toxicity decreases rapidly at 10 ppm.

Table. 5b.

S.N	Complexes/Schiff Base	(%) inhibition after 96 hrs					
		A.flavus			*F.solani*		
		1000 ppm	**100 ppm**	**10 ppm**	**1000 ppm**	**100 ppm**	**10 ppm**
1	[BENDAMB(1,3)$Ni(NCS)_2Cd(SCN)_2$]	65.9	57.3	45.4	74.7	62.2	50.2
2	[BENDAMB(1,3)$Ni(NCS)_2Hg(SCN)_2$]	79.6	64.3	52.1	81.1	75.5	41.0
3	[BENDAMB(1,3)$Hg(NCS)_2Hg(SCN)_2$]	86.4	79.3	58.8	86.1	72.4	52.9

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