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SYNTHESIS, SPECTRAL CHARACTERIZATION AND ANTIMICROBIAL SCREENING OF CO(II), CD(II) AND HG(II) COMPLEXES WITH N, N', - BIS (BENZYLIDENE)-1, 2 – PHENYLENEDIAMINE SCHIFF BASE.

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ABSTRACT

The bimetallic complexes of Co(II), Cd(II) and Hg(II) were synthesized with Schiff base ligand N, N', - Bis (Benzylidene)-1, 2 – Phenylenediamine (BENDAMB 1,2) The structural aspects of these transition metal complexes were determined by elemental analysis, molar conductance, magnetic moment measurements, 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 newly synthesized bimetallic complexes have been screened for their antimicrobial and antifungal activities. and was compared with solvent and Schiff base, screening results indicates that the metal complexes are moderately active compared with those of pure Schiff base, ligand (BENDAMB 1,2).

KEYWORDS: Schiff base, Bimetallic, Antimicrobial activity.

INTRODUCTION

Schiff bases are condensation products of primary amines with carbonyl compounds, they were first reported by Schiff [1] in 1864. The common structural feature of these compounds is azomethine group, which have considerable chemical and biological importance. Due to special property of C=N group, Schiff bases are generally excellent chelating agents.[2-4]

Nowadays, the research field dealing with Schiff base complexes has expanded enormously The importance of Schiff base complexes for bioinorganic chemistry, biomedical applications, supra molecular chemistry has been well recognized and reviewed[5-6], the thiocyanate moiety is reported to have an ability to modify the biochemical behaviour when present in mixed ligand coordination complexes.[7-8]

Bimetallic Schiff base complexes have better biologically activity due to biocompatible metal ions in the complexes.[9-10] In this regard, there is much interest in designing Schiff base ligand and their transition metal complexes. Although several Schiff base derivatives have been reported with different metals, but no systematic approach for the study of that reaction of bimetallic Lewis acid with Schiff base have been made yet so far.

In this paper we have reported on the synthesis, characterization of the of fallowing type of complexes by the reaction of bimetallic Lewis acid $MM'(SCN)_4$ ($M=Co^{2+}$, $M'=Cd^{2+}$, Hg^{2+}) and Schiff base ligand BENDAMB (1, 2) in 1:2 molar ratio.

$$[MM'(SCN_4)]+[BENDAMB(1,2)] \underset{\textbf{1:2}}{\longrightarrow} \left[\begin{array}{c} [(BENDAMB(1,2)_2M(NCS)_2M'(SCN)_4] \\ \text{I} \\ [M(BENDAMB(1,2)_2]^{2+}[M'(SCN)_4]^{2-})] \\ \text{II} \end{array} \right.$$

Furthermore, we also thought that complexes obtained after coupling of biological active Schiff base and bimetallic Lewis acid may prove to possess more microbial activity.

MATERIALS AND METHODS

Solvents were dried and distilled in usual manner Cobalt (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. 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. ^1H –NMR spectra was recorded on Burker DRX-300 in DMSO. The metal and sulphur content were analyzed using standard methods.[11]

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. Cobalt-mercury tetrathiocyanate was used as a standard. Diamagnetic Correction were also made using Pascall's constant.

Preparation of Schiff base:- N,N' –Bis (Benzylidene) -1, 2–phenylenediamine (BENDAMB 1,2)

Schiff base ligand has been prepared by the reaction of Benzaldehyde with 1,2-Phenylenediamine.

The Benzaldehyde and 1, 2-Phenylenediamine were stirred in 2:1 ratio for 8 hrs in water. After constant stirring, a dirty white coloured solid was obtain. It was recrystallized and separated, which gave satisfactory IR, ^{1}H-NMR data and Elemental analyses.

Preparation of Complexes

Metal dithiocyanate were prepared fallowing literature procedure.[12] For the preparation of bimetallic tetrathiocyanate, MM' $(SCN)_4$ Lewis acid solution of $M(SCN)_2$ and $M'(SCN)_2$ were mixed in 1:1 ratio and stirred for 4 hrs, methanolic solution of BENDAMB(1,2) Schiff base was added in 1:2 molar ratio in Lewis acid solution and stirred for 10-18 hrs. In each case a solid was separated which was filtered off and wased with methanol, dried in vacuum and recrystallised 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 nonelectolytic behaviour of complexes Elemental analyses, colour, yield and melting points of the complexes.

TABLE – 1: Elemental analyses, colour, yield & melting point of the complexes.

S.N.	Complexes	Colour	Yield	m.p.	M Co/Cd	M' Cd/Hg	S	Co+ Cd
1	$[(BENDAMB(1,2))_2Co(NCS)_2Cd(SCN)_2]$	Reddish	51	174^{d}	-	-	12.97 (13.19)	17.40 (17.61)
2	$[(BENDAMB(1,2))_2Co(NCS)_2Hg(SCN)_2]$	Brown	46	134	5.37 (5.55)	18.61 (18.91)	11.82 (12.09)	-
3	$[(BENDAMB(1,2))_2Cd(NCS)_2Hg(SCN)_2]$	Brown	45	142	9.91 (10.08)	17.83 (18.00)	11.30 (11.51)	-

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

1.1. Electronic spectra and magnetic moments.

The magnetic moment of the complexes containing Cobalt viz-1 and 2 ranges between 4.36 - 4.70. The Electronic spectra of these complexes show a band between 8050-8090 cm^{-1} which can be assigned for the transition $^4A_2(F)\rightarrow{}^4T_1(F)$ (ν_2) and another band between 16,190-17050 cm^{-1} may be attributed for the transition $^4A_2(F)\rightarrow{}^4T_1(P)$ (ν_3). The electronic spectra of these complexes exhibit two intense bands on higher wave number side, which may easily be assigned as charge transfer bands.

The electronic spectral assignments and magnetic moment of these complexes suggest tetrahedral environment around Cobalt ion.[13] 10 Dq values are in between 4652-4810cm^{-1} and β parameter are between 0.65-0.69 suggesting quite good thermodynamic stability and good co-valency in the complexes. The bimetallic complex containing Cadmium & Mercury ions shows only two intense charge transfer bands, here we suggest tetrahedral geometry around Cadmium & Mercury ion.

1.2. IR spectra analyses

The infrared spectra of these complexes (presented in **Table-2**) exhibit two bands in between 2068-2102cm^{-1} stretching region, clearly indicates the presence of S-bonded terminal SCN group Furthermore, the presence of bands in δ(NCS), ν(C-S), ν(M-N) and ν(M'-S) regions are present at their own position and evident for cationic-anionic structure.

A strong band in the region 1635cm^{-1} appears in Schiff base characteristic of azomethine (>C=N) group.[14-15] This band is shifted towards the lower frequency region (~25-35cm^{-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	$[(BENDAMB(1,2)_2Co(NCS)_2Cd(SCN)_2]$	2071(s);2100(m)	756(m) 781(s)	466(w) 416(m)	1601(s)	311(m)	228(w)	C.A.
2	$[(BENDAMB(1,2)_2Co(NCS)_2Hg(SCN)_2]$	2072(s);2101(m)	747(m) 777(s)	472(w) 410(m)	1600(s)	306(m)	235(w)	C.A
3	$[(BENDAMB(1,2)_2Cd(NCS)_2Hg(SCN)_2]$	2068(m);2104(s)	747(m) 791(sh)	486(w) 412(m)	1604(s)	304(m	230(w)	C.A

1.3. ^{1}H-NMR spectra

The ^{1}H-NMR spectra of the complexes 3 along with ligand were recoded in DMSO given in **Table-3**. The fallowing conclusion can be derived by comparing the spectra of ligand and their corresponding complex.

(1) The ^{1}H NMR spectrum shows a signal δ7.11 due to aromatic ring in the complex.

(2) A protan signal due to -CH=N group appears at δ8.38 in Schiff base, is shifted to downfield and appears at δ8.64 in the complex **3** due to lone pair donation to metal from nitrogen.

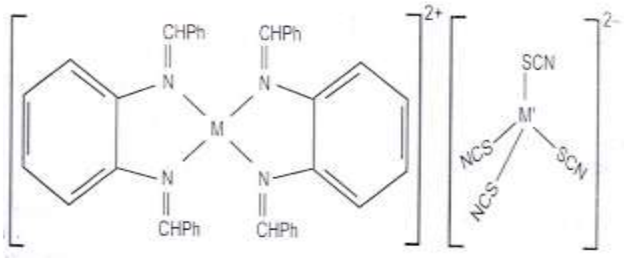
HSAB theory[16] also support the binding possibility of thiocyanate ion in metal complexes 1-3 sulphur end will be attached with soft Cadmium and Mercury metal ions, whereas nitrogen of thiocyanate was well linked with comparatively harder Cobalt.

Therefore on the basis of Electronic spectra, IR spectra and ^{1}H NMR spectra we suggest cationic-anionic structure for the complexes, in which terminal SCN group is present and Schiff base ligand is linked with comparatively harder metal giving rise hard-hard interaction

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

S.N	Complexes	Aromatic ring	-CH=N
1	BENDAMB(1, 2)	7.17(s) 7.46(m)	8.38
2	[(BENDAMB(1,2)$_2$Cd(NCS)$_2$Hg(SCN)$_2$]	7.11(s) 7.53(m)	8.64 (m)

Structure - A



(B)

$M = Co^{2+}, Ni^{2+}, Cd^{2+}; \quad M' = Cd^{2+}, Hg^{2+}$

Fig. 5.2

1.4. Application of softness parameter to the nature of bridge

By using Klopmann quantum mech.[17] procedure the softness values of bimetallic complexes have been calculated since these values are related with nature of complexes.

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 quite high ranges in between 40.34-44.56 which can be accounted for cationic-anionic 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	$[(BENDAMB(1,2)_2Co(NCS)_2Cd(SCN)_2]$	41.36	C.A
2	$[(BENDAMB(1,2)_2Co(NCS)_2Hg(SCN)_2]$	44.56	C.A
3	$[(BENDAMB(1,2)_2Cd(NCS)_2Hg(SCN)_2]$	44.34	C.A

ANTIMICROBIAL AND ANTIFUNGAL ACTIVITIES

(a) **Antibacterial activity**

Schiff base ligand and their complexes were screened to evaluate their antibacterial activity against bacteria (***E.coli***, ***P.aurginisa***). All the complexes shows superior activity compared to Schiff base and 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	Schiff base	+	+
3	$[(BENDAMB(1,2)_2Co(NCS)_2Cd(SCN)_2]$	++	+
4	$[(BENDAMB(1,2)_2Co(NCS)_2Hg(SCN)_2]$	++	++
5	$[(BENDAMB(1,2)_2Cd(NCS)_2Hg(SCN)_2]$	+++	++

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

(b) Antifungal activity

The fungicidal activity of the complexes with Schiff bases 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 96hr by various compound was calculated by from the expression given below.

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

Where C = diameter of fungus colony in control plates after 96hr and T = diameter of fungus colony in tested plated after 96hr. The results compiled in Table -**5b**, indicates that all the complexes were more active than their corresponding Schiff bases, probably due to their more lipopilic character and they 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(1,2)]	77.4	53.9	39.4	75.8	57.7	34.4
2	[(BENDAMB(1,2)$_2$Co(NCS)$_2$Cd(SCN)$_2$]	93.7	79.7	54.7	91.3	86.9	50.2
3	[(BENDAMB(1,2)$_2$Co(NCS)$_2$Hg(SCN)$_2$]	97.2	66.8	54.6	88.3	62.9	41.0
4	[(BENDAMB(1,2)$_2$Cd(NCS)$_2$Hg(SCN)$_2$]	99.4	79.6	49.3	94.4	69.1	44.4

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