

Synthesis, Characterization and Biological Studies of Bimetallic Complexes Containing Co(II), Cd(II) and Hg(II) and {N, N', -Bis (Benzylidene)-1,3 Phenylene-Diamine} Schiff Base, in 1:2 Ratio

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Abstract

A new series of bimetallic complexes of, Co (II), Cd (II) and Hg (II) with Schiff base ligand (N, N', -Bis (Benzylidene) -1,3 -Phenylenediamine, {BENDAMB (1,3)}) have been synthesized and characterized by elemental analysis, molar conductance, magnetic moment measurements, IR, Electronic and ^1H NMR spectral studies. The softness parameter $TE_n^\#$ of complexes have also been calculated to derive the binding site of the thiocyanate ligand. The spectral data shows that the Schiff base ligand is linked with comparatively harder metal Co^{2+} whereas SCN present as terminal. Magnetic susceptibility measurements indicate tetrahedral geometry around Cobalt ion. The softness parameter, suggest cationic- anionic structure for these complexes. 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, BENDAMB (1, 3)

Keywords: Schiff base, Bimetallic, Antimicrobial activity

Introduction

Bi-dentate Schiff bases are well known to co-ordinate with various metal ions and have attracted a great deal of interest in recent years due to their rich co-ordination chemistry of $-\text{C}=\text{N}$ group (azomethine), they are used as chelating ligand in coordination chemistry of transition metals.¹⁻²

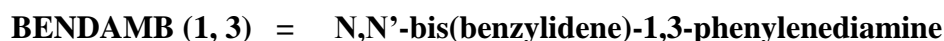
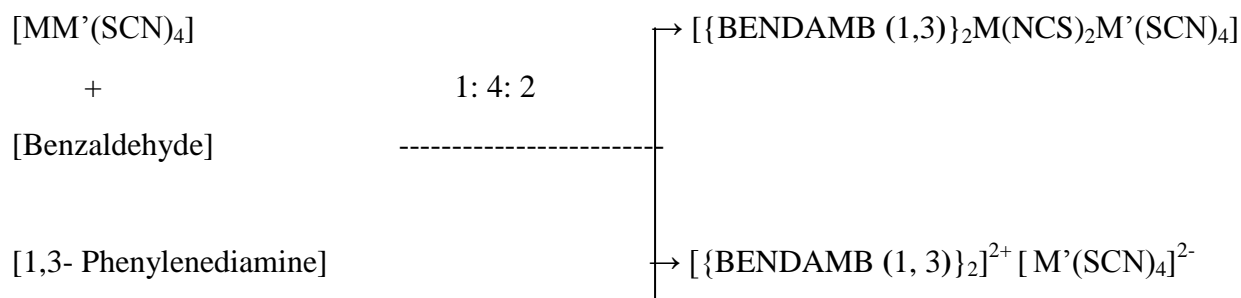
Due to their relatively simple synthesis and structural diversity Schiff bases and their metal complexes have been shown to be promising leads for both synthetic and structural research and due to their incredible chemical properties and applications in various areas they have been widely investigated.³⁻⁴

The importance of Schiff base complexes for bioinorganic chemistry, biomedical applications, supra molecular chemistry has been well recognized and reviewed, they show antibacterial, antifungal and herbicidal activity.⁵⁻⁶

Bimetallic Schiff base, complexes have better biological activity due to biocompatible metal ions in the complexes.⁷⁻⁸

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 activity of hetro-bimetallic complexes of the following type.



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 ⁹. 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^oK. 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 Bimetallic Complexes

Bimetallic complexes of N, N'- bis (benzylidene)-1,3-phenylenediamine, [BENDAMB(1,3)] Schiff base were synthesized by template method ¹⁰. Metal dithiocyanate were prepared by following literature procedure ¹¹, 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 (4 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 5-6 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 recrystallised from Acetone/Chloroform.

All bimetallic complexes were partially/completely soluble in DMSO

Results and Discussion

The Elemental analyses, Color, Yield and Melting points of the complexes presented in

Table-1, Stoichiometry of the complexes, are in agreement with elemental analyses the lower value of conductance in DMSO is indicative of non-electrolytic behaviour of complexes.

Table - 1

Elemental analyses, color, yield & melting point of the complexes

S.N	Complexes	Color	Yield	M.P	M Co/Cd	M' Cd/Hg	S	Co+ Cd
1	[{BENDAMB(1,3)} ₂ Co(NCS) ₂ Cd(SCN) ₂]	Reddish	46	171 ^d	-	-	13.01 (13.19)	17.38 (17.61)
2	[{BENDAMB(1,3)} ₂ Co(NCS) ₂ Hg(SCN) ₂]	Light Brown	61	140	5.40 (5.55)	18.60 (18.91)	11.72 (12.09)	-
3	[{BENDAMB(1,3)} ₂ Cd(NCS) ₂ Hg(SCN) ₂]	Dirty white	46	141 ^d	9.91 (10.08)	17.80 (18.00)	11.36 (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, 4.44 – 4.77 BM. The Electronic spectra of these complexes show a band between 8056-8083 cm⁻¹ which can be assigned for the transition 4A₂(F) → 4T₁(F) (□□) and another band between 16,830-17010 cm⁻¹ may be attributed for the transition 4A₂(F) → 4T₁(P) (□□). 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 ion¹². 10 Dq values are in between 4652-4776 cm⁻¹ and □ parameter are between 0.63-0.67 suggesting quite good thermodynamic stability and good co-valency in the complexes.

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 2069-2108 cm⁻¹ clearly indicates the presence of S-bonded terminal SCN groups. The presence of other bands □(NCS), □(C-S), □(M-N) and □(M'-S) are appeared at their own position and favour cationic- anionic structure for these complexes.

A strong band in the region 1633cm⁻¹ appears in Schiff base characteristic of azomethine (>C=N) group¹³. This band is shifted towards the lower frequency region appeared in the region (□ □ □ □ 1604 cm⁻¹) in the bimetallic complexes, indicative of coordination of the Schiff base azomethine nitrogen atoms.

Table - 2

S.N.	Complexes	C-N (Str)	C-S (Str)	□N CS (ben d)	>C=N(Str) azomethine	□(M-N)	□(M'-S)	Structure

1	$[\{BENDAMB(1,3)\}_2Co(NCS)_2Cd(SCN)]$	2069(s);2103(m)	756(m);778(s)	472(w) 420(m)	1604(s)	301(m)	239(w)	C.A.
2	$[\{BENDAMB(1,3)\}_2Co(NCS)_2Hg(SCN)]$	2071(s);2092(sh)	751(m);781(s)	481(w) 415(m)	1597(s)	314(m)	235(w)	C.A.
3	$[\{BENDAMB(1,3)\}_2Cd(NCS)_2Hg(SCN)]$	2070(m);2108(m)	747(m);790(s)	486(w) 439(m)	1596(s)	304(m)	231(w)	C.A.

1.3. 1H -NMR spectra

The 1H -NMR spectra of the complexes 3 recorded in DMSO given in **Table-3**. The following conclusion can be derived.

- (1) The 1H NMR spectrum shows a signal \square 7.17 due to aromatic ring in the complex.
- (2) A proton signal due to $-CH=N$ group appears at \square 8.64 in the complex **3** due to lone pair donation to metal from nitrogen.

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

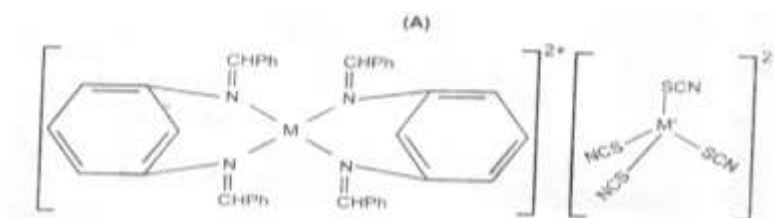
S.N	Complexes	Aromatic ring	-CH=N
1	$[\{BENDAMB(1,3)\}_2Cd(NCS)_2Hg(SCN)]$	7.17(s) 7.63(m)	8.64(s)

For above complexes we suggest cationic - anionic structure, in which Schiff base ligand linked with comparatively harder metal giving rise to hard- hard interaction and SCN present as terminal.

Cationic- anionic structure (A) for the complexes also supported by the following grounds,

- a) The complexes containing Cobalt metal viz-1 and 2, has higher 10Dq value which indicate the presence of bridged NCS group.
- b) HSAB theory¹⁴ 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.

Structure - A



1.4. Application of softness parameter to the nature of bridge

Quantitative softness value of M and M' (M=Co; M' =Cd, Hg) and thiocyanate ion are related with nature of the complexes i.e. cationic - anionic. These softness values are derived by quantum mechanical procedure pioneered by Klopman.¹⁵

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 $TE_n^{\square}(M-M')$ for complexes 1, 2, 3 are in between 41.81- 43.06 which can be accounted for cationic - anionic structure. The $TE_n^{\square}(M-M')$ values and predictions are presented in, **Table-4**

Table – 4

S.N	Complexes	$TE_n^{\square}(M-M')$	Nature of Bridge
1	$[\{BENDAMB(1,3)\}_2Co(NCS)_2Cd(SCN)_2]$	43.06	C.A.
2	$[\{BENDAMB(1,3)\}_2Co(NCS)_2Hg(SCN)_2]$	41.81	C.A.
3	$[\{BENDAMB(1,3)\}_2Cd(NCS)_2Hg(SCN)_2]$	42.87	C.A.

Antimicrobial and Antifungal Activities

(a) **Antibacterial activity** – Complexes were screened to evaluate their antibacterial activity against bacteria (*E.coli*, *P.auriginisa*). All the complexes shows superior activity compared to solvent, which can be explained on the basis of Tweedy theory¹⁶ 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	<i>E.coli</i>	<i>P.auriginisa</i>
1	DMSO	-	-
2	$[\{BENDAMB(1,3)\}_2Co(NCS)_2Cd(SCN)_2]$	++	+
3	$[\{BENDAMB(1,3)\}_2Co(NCS)_2Hg(SCN)_2]$	++	++
4	$[\{BENDAMB(1,3)\}_2Cd(NCS)_2Hg(SCN)_2]$	+++	++

(-) 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 compounds was calculated from the given, expression –

$$(\%) \text{ inhibition} = 10 (C-T) / C$$

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					
		<i>A.flavus</i>			<i>F.solani</i>		
		1000 ppm	100 ppm	10 ppm	1000 ppm	100 ppm	10 ppm
1	[{BENDAMB(1,3)} ₂ Co(NCS) ₂ Cd(SCN) ₂]	64.3	60.3	45.2	83.5	73.5	50.2
2	[{BENDAMB(1,3)} ₂ Co(NCS) ₂ Hg(SCN) ₂]	85.2	76.4	56.1	86.7	77.5	43.5
3	[{BENDAMB(1,3)} ₂ Cd(NCS) ₂ Hg(SCN) ₂]	81.6	77.3	42.8	89.5	60.4	40.3

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