

# Synthesis, Characterization, Antifungal and Insecticidal Studies of Some Thiocyanato-Bridged Bimetallic Complexes Containing Ni(II), Cd(II), Hg(II) & *N, N'*-Bis(benzylidene) 1, 2-phenylenediamine Schiff Base

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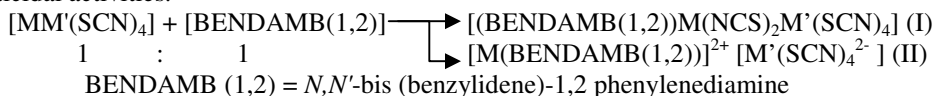
**Abstract:** *N, N'*-bis(benzylidene)-1,2-phenylenediamine Schiff base was prepared by the reaction of benzaldehyde with 1,2 phenylenediamine and its complexes of molecular formula  $[MM'(SCN)_4(BENDAMB)(1, 2)]$  ( $M = Ni^{2+}$ ;  $M' = Cd^{2+}, Hg^{2+}$ ) have been synthesized and characterized by elemental analyses, conductance measurement and various spectral studies. On the basis of softness parameter, spectral and magnetic studies monomeric bridged structure suggested for all the complexes. The antifungal activity against *A.flaus*, *F.solani* and Insecticidal screening against Red cotton bug (*Dysdercus koenigii*) of complexes has been done which shows good results.

**Keywords:** Bimetallic, Thiocyanato, Schiff base

## Introduction

Transition metal complexes have been widely explored because of their catalytic property and versatile biological activities including antifungal and insecticidal activities<sup>1,2</sup>, while Schiff bases are good ligands and shows chemical reactivity and various biological activities<sup>3-4</sup> when mixed with bimetallic Lewis acid  $MM'(SCN)_4$  ( $M=Ni^{2+}$ ,  $M'=Cd^{2+}, Hg^{2+}$ ). Binding mode sensitivity of thiocyanate ion has attained great interest in recent years. The thiocyanate moiety is reported to have an ability to modify the biochemical behaviour when present in mixed ligand coordination complexes<sup>5-6</sup>.

The main aim of present work was to synthesis and characteriszed thiocyanato bridged bimetallic complexes of Ni(II), Cd(II) and Hg(II) and to study their antifungal and insecticidal activities.



## Experimental

All the chemicals used for synthesizing Schiff base and its complexes were of A.R grade. The solvents used were purified by distillation. The potassium thiocyanate was used after drying in vacuum.

### Preparation of Schiff base

#### *N,N'*-Bis(benzylidene)-1, 2-phenylenediamine (BENDAMB)

Schiff base ligand (BENDAMB) was prepared by the reaction of benzaldehyde with 1,2-phenylenediamine as reported earlier<sup>7</sup>.

#### Preparation of complexes

Metal dithiocyanate were prepared as per literature procedure<sup>8</sup>. For the preparation of bimetallic tetrathiocyanate MM' (SCN)<sub>4</sub> (Lewis acid), a solution of M(SCN)<sub>2</sub> and M'(SCN)<sub>2</sub> were mixed in 1:1 ratio and stirred for 4 h, methanolic solution of BENDAMB(1,2) Schiff base was added in 1:1 molar ratio in Lewis acid solution and stirred for 10-18 h. In each case a solid was separated which was filtered off and washed with methanol, dried in vacuum and recrystallised from acetone/chloroform. For the preparation of homobimetallic mercury complex, a slight different procedure was adopted. To a solution/slurry of Hg(SCN)<sub>2</sub> in methanolic solution of Schiff base BENDAMB (1,2) was added in 1:1 molar ratio and stirred for 2 h and then 1 mole of methanolic solution of Hg(SCN)<sub>2</sub> was added to the above solution and stirred for 16 h. A grey coloured solid was formed, which was filtered off, washed with methanol and dried in vacuum and recrystallized in acetone/chloroform. All bimetallic complexes were partially/completely soluble in DMSO.

## Results 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 nonelectrolytic behaviour of complexes.

**Table 1.** Elemental analyses, colour, yield and melting point of the complexes

S.No.	Complexes	Colour	Yield	M.P.	M %, Actual value (Calcd.)		
					Ni	Cd/Hg	S
1	[BENDAMB(1,2)Ni(NCS) <sub>2</sub> Cd(SCN) <sub>2</sub> ]	Light grey	41	142 <sup>d</sup>	8.31 (8.53)	16.24 (16.34)	18.36 (18.64)
2	[BENDAMB(1,2)Ni(NCS) <sub>2</sub> Hg(SCN) <sub>2</sub> ]	Grey	62	149 <sup>d</sup>	7.33 (7.56)	25.61 (25.85)	16.30 (16.52)
3	[BENDAMB(1,2)Hg(NCS) <sub>2</sub> Hg(SCN) <sub>2</sub> ]	Yellow	56	159 <sup>d</sup>	-	43.38 (43.70)	13.69 (13.97)

*d-decompose*

### Elemental spectra and magnetic moments

All these complexes are diamagnetic in nature. The electronic spectra of these complexes show a band between 24800-25200 cm<sup>-1</sup> which can be assigned for the transition <sup>1</sup>A<sub>1</sub>(g)→<sup>1</sup>B<sub>1</sub>(g) (ν<sub>1</sub>) and another band between 30840-31700 cm<sup>-1</sup> may be attributed for the transition <sup>1</sup>A<sub>1</sub>(g)→<sup>1</sup>B<sub>1</sub>(g) (ν<sub>2</sub>). A charge transfer band has also been observed for these complexes. All assignments are in favour of square planar geometry for nickel ion<sup>9-10</sup>.

### IR spectra analyses

The infrared spectra of these complexes (Table 2) exhibit four bands in -C-N stretching region

The presence of two bands in between 2110-2158  $\text{cm}^{-1}$  clearly indicates the presence of thiocyanate as bridging unit. Similarly the presence of two characteristic  $\nu(\text{CN})$  bands for *S*-bonded terminal SCN furthermore, the presence of bands in  $\delta(\text{NCS})$ ,  $\nu(\text{C-S})$ ,  $\nu(\text{M-N})$  and  $\nu(\text{M'-S})$  regions are diagnostic for the nature of thiocyanate bonding<sup>8</sup>.

All the assignments are in favour of monomeric bridge structure for these complexes. A strong band in the region 1635  $\text{cm}^{-1}$  appears in Schiff base characteristic of azomethine ( $>\text{C}=\text{N}$ ) group<sup>11-12</sup>. This band is shifted towards the lower frequency region ( $\sim 20\text{-}30 \text{ cm}^{-1}$ ) in the bimetallic complexes indicative of Schiff base azomethine nitrogen atoms.

**Table 2.** IR spectral data of the complexes

S. No.	Complexes	C-N (Str)	C-S (Str)	$\delta\text{NCS}$ (bend)	$>\text{C}=\text{N}(\text{Str})$ azomethine	$\nu(\text{M-N})$	$\nu(\text{M'-S})$	Str
1	[BENDAMB (1,2)Ni(NCS) <sub>2</sub> Cd(SCN) <sub>2</sub> ]	2112(sh);2 158(s) 2070(s);20 80(w)	738(m); 769(s) 719(sh)	481(w) 419(m)	1598(s)	310(m)	226(w)	M.B
2	[BENDAMB (1,2)Ni(NCS) <sub>2</sub> Hg(SCN) <sub>2</sub> ]	2110(sh);2 151(s) 2072(s);20 95(w)	746(m); 769(s) 741(sh)	483(w) 418(m)	1590(s)	305(m)	233(w)	M.B
3	[BENDAMB (1,2)Hg(NCS) <sub>2</sub> Hg(SCN) <sub>2</sub> ]	2116(sh);2 152(s) 2091(s);21 04(m)	738(m); 786(s) 727(sh)	502(w) 477(m)	1609(s)	301(m)	238(w)	M.B

### <sup>1</sup>H NMR spectra

The <sup>1</sup>H NMR spectra of the diamagnetic complexes *viz* 1- 3 along with ligand were recorded in DMSO (Table 3). The following conclusion can be derived by comparing the spectra of ligand and their corresponding complex.

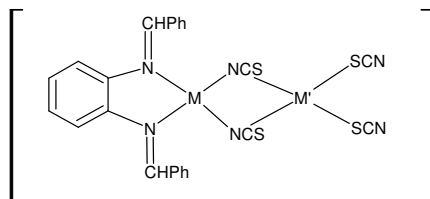
- (1) The <sup>1</sup>H NMR spectra shows a signal between  $\delta 7.14\text{-}7.66$  due to aromatic ring in the complexes.
- (2) A proton signal due to  $-\text{CH}=\text{N}$  group appears at  $\delta 8.38$  in Schiff base, is shifted to downfield and appears between  $\delta 8.67\text{-}8.80$  probably due to lone pair donation to metal from nitrogen.

**Table 3.** <sup>1</sup>H NMR data (ppm) of the complexes

S.No.	Complexes /Ligand	Aromatic ring	$-\text{CH}=\text{N}$
1	BENDAMB(1, 2)	7.17(s) , 7.46(m)	8.38
2	[BENDAMB(1,2)Ni(NCS) <sub>2</sub> Cd(SCN) <sub>2</sub> ]	7.55(s) , 7.19(m)	8.72(s)
3	[BENDAMB(1,2)Ni(NCS) <sub>2</sub> Hg(SCN) <sub>2</sub> ]	7.14(s) , 7.66(m)	8.80(m)
4	[BENDAMB(1,2)Hg(NCS) <sub>2</sub> Hg(SCN) <sub>2</sub> ]	7.19(s) , 7.33(m)	8.67(m)

Therefore on the basis of electronic spectra, IR spectra and <sup>1</sup>H NMR spectra, we suggest monomeric bridged structure (A) for the complexes, in which SCN from bridge between two metals and Schiff base ligand is linked with comparatively harder metal like Ni<sup>2+</sup>. Monomeric bridged structure (A) for the complexes 1,2,3 are also supported by the following ground.

- (a) Since nickel complexes are low spin, it is clear that it is not surrounded by four NCS group because the  $[\text{Ni}(\text{NCS})_4]^{2-}$  ion is high spin<sup>13</sup>.
- (b) HSAB theory<sup>14</sup> 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.



#### 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<sup>15</sup>.

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  $\text{TE}n^\ddagger(\text{M}-\text{M}')$  for complexes 1, 2, 3 are in between 19.08-22.08 which can be accounted for monomeric bridged structure. The  $\text{TE}n^\ddagger(\text{M}-\text{M}')$  values and predictions are presented in Table 4.

**Table 4.** Softness values & predictions

S.No.	Complexes	$\text{TE}n^\ddagger(\text{M}-\text{M}')$	Nature of bridge
1	[BENDAMB(1,2)Ni(NCS) <sub>2</sub> Cd(SCN) <sub>2</sub> ]	22.08	M.B
2	[BENDAMB(1,2)Ni(NCS) <sub>2</sub> Hg(SCN) <sub>2</sub> ]	20.11	M.B
3	[BENDAMB(1,2)Hg(NCS) <sub>2</sub> Hg(SCN) <sub>2</sub> ]	19.08	M.B

#### Antifungal and insecticidal studies

Insecticidal and antifungal screening of these complexes has been done.

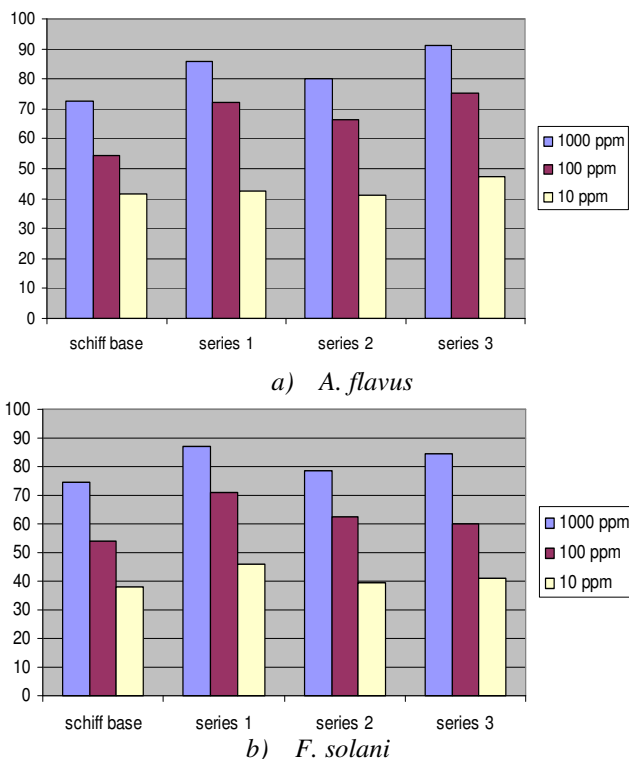
##### Insecticidal experiments

0.1% Solution (in DMSO) of complex 1, 2 and 3 were tested for insecticidal activity against red cotton bug (*Dysdercus koewgii*) by contact poison technique. It can be observed that the synergic effect of complex and solvent have greater lethality than the additive lithal effect of the Schiff base ligand and the solvent. This is probably due to toxic effect of mercury/cadmium and thiocyanate moiety. Therefore it can be concluded that the Schiff base coupled with bimetallic Lewis acid; proved to have enhanced lethal effect on insects.

##### Antifungal screening

The fungicidal activity of the complexes with Schiff bases was evaluated against *A.flavus* and *F. solani* by Agar plate technique at three concentrations (1000 ppm, 100 ppm and 10 ppm). The average percentage inhibition after 96 h 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 h and T = diameter of fungus colony in tested plated after 96 h. The results were plotted in a bar diagram (Figure 1).



**Figure 1.** Fungicidal activity of the complexes with Schiff bases against; a) *A. flavus* & b) *F. solani* by Agar plate technique at 1000 ppm, 100 ppm and 10 ppm

All the complexes were more active than their corresponding Schiff bases, probably due to their more lipophilic character and they show significant toxicity at 1000 ppm and 100 ppm but toxicity decreases rapidly at 10 ppm

## Conclusion

*N,N'*-Bis(benzylidene)-1,2-phenylenediamine Schiff base used as ligand to synthesis thiocyanato bridged bimetallic complexes of Ni(II), Cd(II), Hg(II). These complexes are diamagnetic in nature and have monomeric bridged structure. From the antifungal / insecticidal results we can say that Homobimetallic mercury complex shows significant activity while other two complexes show moderate activity.

## References

1. Lukyanenko N G, Pastushok V N and Bordunov A V, *Synthesis*, 1991, 241.
2. Ahmed A A, Benguzzi S A and Hadi A A, *J Sci Appl.*, 2007, 79.
3. Singh H, Shukla S N and Srivastava R S, *Bull Soc Chim Fri.*, 1991, **128**, 530-536.
4. Shukla S N, Khan Sadique, Upadhyay N, Manikpuri N, Jain S.K and Srivastava A, *Oriental J Chem.*, 2006, **22(2)**, 305-314.
5. Kinoshita H, Shimoi M, Ouchi A and Santo S, *Bull Chem Soc Jpn.*, 1986, **59**, 1253.
6. Shukla S N, Nigam H K, Upadhyay N, Khan S and Srivastava A, *J Appl Biosci.*, 2006, **32(1)**, 68-73.

7. Upadhayay N, *Chem Sci Trans.*, 2013, **2(2)**, 455-460.
8. Singh P P, Yadav S P and Sharma S B, *Aust J Chem.*, 1977, **30**, 1921.
9. Lever A B P, *Inorganic Electronic Spectroscopy*, Elsevier, New York, 1955, 280.
10. Maki G, *J Chem Phys.*, 1958, **28**, 651.
11. Biradar N S, Roddabasanagoudar V L and Aminabhavi T M, *Polyhedron*, 1984, **3(5)**, 575.
12. Desmukh K K, Hundekar A M and Sen D N, *J Indian Chem Soc.*, 1980, **57**, 1147.
13. Foster D and Goodgame D M L, *Inorg Chem.*, 1965, **4(6)**, 823-829.
14. Pearson R G, *J Am Chem Soc.*, 1965, **85**, 3533.
15. Klopman G, *J Am Chem Soc.*, 1968, **90**, 223.