Synthesis, Characterization and Biological Studies of Some Thiocyanato-bridged Bimetallic Complexes Containing Co(II), Cd(II), Hg(II) and *N, N'*-Bis(benzylidene)-1,2-phenylene-diamine Schiff Base

N. UPADHAYAY

Department of Chemistry, Pt. SNS Govt. PG College, Shahdol-(M P), India
drnavin_upa@yahoo.com

Abstract: The coordination chemistry of transition metal complexes has been progressing at a tremendous pace. These complexes were finding use in the field of homogeneous catalysis, analytical chemistry and biological system. The presence of thiocyanto group in mixed ligand coordinated complexes of transition metal was reported to have an ability to influence the biochemical behaviour of the complexes. Complexes of $MM'(SCN)_4$ ($M = Co^{2+}$; $M' = Cd^{2+}$, Hg^{2+}) with *N, N'*–bis (benzylidene) -1, 2, phenylenediamine Schiff base of molecular formula $[MM'(SCN)_4(BENDAMB) (1, 2)]$ have been synthesized and characterized by elemental analyses, molar conductance magnetic moment, IR, electronic and ^1H NMR spectral studies. The softness parameter $TEn^{\neq}$ of complexes have also been calculated to derive the binding side of the thiocyanate ligand. The insecticidal activity against Red cotton bug (*Dysdercus koenigii*) and antifungal activity against *A.Flavus* and *F.Solani* of complexes also been investigated and was compared with solvent and Schiff base.
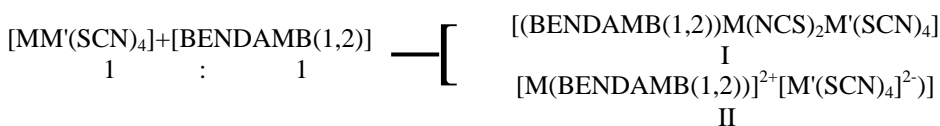
Introduction

Chemistry of Schiff base and their metal complexes became a subject of great interest due to their diversified application. These Schiff base complexes were finding use in various fields like pharmaceutical-industry, agriculture and organic synthesis[1-3].

Some Schiff base metal chelates of transition metal ion were used as nuclear medicine and some even possess anti-cancer activity[4-5]. Binding mode sensitivity of thiocyanate ion has attained great interest in recent years. The thiocyanate moiety was reported to have an ability to modify the biochemical behaviour when present in mixed ligand coordination complexes[6-7].

Recently, growth of $[CdHg(SCN)_4(H_6C_2OS)_2]$ cadmium mercury thiocyanate dimethyl sulfoxide an arganometallic nonlinear optical (NLO) complex crystal gave a new look to the study of bimetallic complexes[8]. Bimetallic thiocyanate complexes like $CdHg(SCN)_4$ and $MnHg(SCN)_4$ have given a new dimension to the study of nonlinear optical crystal[9-11].

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. Encouraged from our results with *N,N'*-bis (salicylidene)-1, 2 ethylenediamine and with *N,N'*-bis (benzylidene)-1,2-ethylenediamine[12-13], we prone to synthesize the complex of fallowing type by the reaction of bimetallic Lewis acid MM'(SCN)$_4$ (M=Co^{2+}, M'=Cd^{2+}, Hg^{2+}) and Schiff base BENDAMB (1, 2) in 1:1 molar ratio.

Furthermore, we also thought that complexes obtained after coupling of biological active Schiff base and bimetallic Lewis acid may prove to possess more biological activity. Keeping in view that such a study would be more illuminating in terms of structural assignment, chemical reactivities and biological activity of the complexes formed, the present study was undertaken.

$$[MM'(SCN)_4]+[BENDAMB(1,2)] \longrightarrow \begin{bmatrix} [(BENDAMB(1,2))M(NCS)_2M'(SCN)_4] \\ I \\ [M(BENDAMB(1,2))]^{2+}[M'(SCN)_4]^{2-})] \\ II \end{bmatrix}$$

$$1 \quad : \quad 1$$

BENDAMB (1,2) =*N,N'*-bis (benzylidene)-1,2 phenylenediamine

Experimental

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. ^{1}H NMR spectra was recorded on Burker DRX-300 in DMSO. The metal and sulphur content were analyzed using standard methods[14].

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 ^{0}K. 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)

Schiff base ligand has been prepared by the reaction of benzaldehyde with 1,2-phenylene-diamine. The benzaldehyde and 1, 2-phenylenediamine were stirred in 2:1 ratio for 8 h in water. After constant stirring, a dirty white coloured solid was obtained. It was recrystallised and separated, which gave satisfactory IR, ^{1}H NMR data and elemental analyses.

Preparation of complexes

Metal dithiocyanate were prepared following literature procedure[15]. 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 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. All bimettalic complexes were partially/ completely soluble in DMSO.

Results and Discussion

The stoichiometry of the complexes are in good 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 and melting point of the complexes

No.	Complexes	Colour	Yield	m.p.	M Co/Cd	M' Cd/Hg	S	Co+ Cd
1	[BENDAMB(1,2) Co(NCS)$_2$Cd(SCN)$_2$]	Blue	43	162^d	-	-	18.49 (18.64)	24.72 (24.89)
2	[BENDAMB(1,2) Co(NCS)$_2$Hg(SCN)$_2$]	Light grey	52	143^d	7.32 (7.59)	25.63 (25.84)	16.41 (16.52)	-
3	[BENDAMB(1,2) Cd(NCS)$_2$Hg(SCN)$_2$]	Dark brown	42	163^d	13.36 (13.54)	23.97 (24.70)	15.24 (15.45)	-

d-decompose

Elemental spectra and magnetic moments

The magnetic moment of the cobalt complexes **1** and **2** are ranges between 4.42-4.80. The electronic spectra of these complexes show a band between 8045-8056 cm^{-1} which can be assigned for the transition $4A_2(F) \rightarrow 4T_1(F)$ (ν_2) and another band between 16,460-16950 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[16]. 10 Dq values are in between 4990-4995 cm^{-1} and β parameter are between 0.68-0.69 suggesting quite good thermodynamic stability and good co-valency in the complexes.

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 2105-2160 cm^{-1} clearly indicates the presence of thiocyanate as bridging unit. Similarly the presence of two characteristic $\nu(CN)$ bands for *S*-bonded terminal SCN. Furthermore, the presence of bands in $\delta(NCS)$, $\nu(C-S)$, $\nu(M-N)$ and $\nu(M'-S)$ regions are diagnostic for the nature of thiocyanate bonding[15].

All the assignments are in favour of monomeric bridge structure for these complexes. A strong band in the region 1635 cm^{-1} appears in Schiff base characteristic of azomethine (>C=N) group[17-18]. This band is shifted towards the lower frequency region (~20-30 cm^{-1}) in the bimetallic complexes indicative of Schiff base azomethine nitrogen atoms.

^1H 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 δ7.13 due to aromatic ring in the complex.

(2) A proton signal due to -CH=N group appears at δ8.38 in Schiff base, is shifted to downfield and appears at δ8.71 in the complex **3** due to lone pair donation to metal from nitrogen.

Table 2. IR spectral data of complexes

S. No.	Complexes	C-N (Str)	C-S (Str)	δNCS (bend)	>C=N(Str) azomethine	ν(M-N)	ν(M'-S)	Structure
1	[BENDAMB(1,2) Co(NCS)₂Cd(SCN)₂]	2105(sh);2145(s) 2067(s); 2088(w)	748(m); 781(s) 717(sh)	468(w) 442(m)	1604(s)	301 (m)	234 (w)	M.B
2	[BENDAMB(1,2) Co(NCS)₂Hg(SCN)₂]	2114(sh); 2144(s) 2077(s); 2090(w)	756(m); 781(s) 721(sh)	479(w) 415(m)	1595(s)	304 (m)	234 (w)	M.B
3	[BENDAMB(1,2) Cd(NCS)₂Hg(SCN)₂]	2110(sh); 2160(s) 2075(s); 2104(m)	743(m); 787(s) 711(sh)	487(w) 423(m)	1598(s)	314 (m	227 (w)	M.B

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

S.No.	Complexes	Aromatic ring	-CH=N
1	BENDAMB(1, 2)	7.17(s) 7.46(m)	8.38
2	[BENDAMB(1,2)Cd(NCS)₂Hg(SCN)₂]	7.13(s) 7.49(m)	8.71(s)

Therefore on the basis of electronic spectra, IR spectra and ^{1}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 Co^{2+}.

(A)
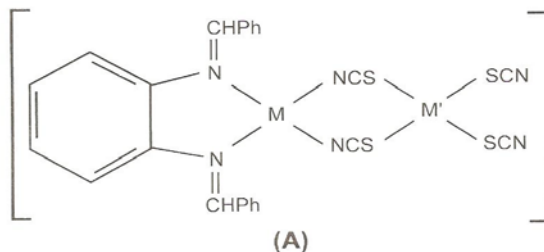
Monomeric bridged structure (A) for the complexes **1, 2, 3** are also supported by the fallowing aspects.

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

(b) HSAB theory[19] 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.

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* monomeric bridged. These softness values are derived by quantum mechanical procedure pioneered by Klopman[20].

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 21.33-28.63 which can be accounted for monomeric bridged structure. The $TEn^{\neq}$ (M-M') values and predictions are presented in Table 4.

Table 4. Softness values and predictions

S.N	Complexes	$TEn^{\neq}$ (M-M')	Nature of Bridge
1	[BENDAMB(1,2)Co(NCS)$_2$Cd(SCN)$_2$]	28.63	M.B
2	[BENDAMB(1,2)Co(NCS)$_2$Hg(SCN)$_2$]	21.33	M.B
3	[BENDAMB(1,2)Cd(NCS)$_2$Hg(SCN)$_2$]	23.36	M.B

Biological studies

Biological activities of these complexes were tested for insecticidal and antifungal screening.

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 lethal 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 the three concentration 1000 ppm, 100 ppm and 10 ppm. The average percentage inhibition after 96 h by various compounds was calculated from the expression given below.

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

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 compiled in Table 5, indicates that 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.

Table 5. Antifungal screening data

S.No	Complexes/Schiff Base	% Inhibition after 96 h					
		A.flavus			*F.solani*		
		1000 ppm	100 ppm	10 ppm	1000 ppm	100 ppm	10 ppm
1	[BENDAMB(1,2)]	72.4	54.3	41.6	74.3	54.1	38.2
2	[BENDAMB(1,2)Co(NCS)$_2$Cd(SCN)$_2$]	89.7	78.3	46.4	93.3	84.2	45.2
3	[BENDAMB(1,2)Co(NCS)$_2$Hg(SCN)$_2$]	87.2	69.6	46.9	88.4	60.6	37.5
4	[BENDAMB(1,2)Cd(NCS)$_2$Hg(SCN)$_2$]	92.4	74.3	48.3	89.6	62.4	42.4

Conclusion

It can be concluded that bimetallic complexes synthesized by the reaction of bimetallic Lewis acid with Schiff base shows non-electolytic nature, all these complexes have monomeric bridged structure in which SCN form bridge between two metals and Schiff base ligand is linked with metals by coordinate bond. Complexes containing cadmium/mercury shows more toxic effect against insects and against fungus than Schiff base.

References

1.   Hartley F R, Burgess C J and Alcock R M, In Solution Equilibrium; New York, 1980.
2.   Dhar D N and Taploo C L, *J Sci Indust Res*., 1982, **41**, 501-506.
3.   Singh H, Shukla S N and Srivastava R S, *Bull Soc Chim Fri.,* 1991, **128**, 530-536.
4.   Benoist F, Genstin J F, Blanchared P, Jabault M and Quintard J P, *Transition Met Chem.,* 1999, **24**, 42-48.
5.   Sharma K P, Jolly V S and Pathak P, *Ultra Sci Phys Sci*., 1998, **10**, 263-266.
6.   Kinoshila H, Shimoi M, Ouchi A and Santo S, *Bull Chem Soc Jpn.,* 1986, **59,** 1253.
7.   Singh H, Shukla S N and Srivastava R S, *Bull Soc Chim Fr*., 1991, **128**, 530-536.
8.   Shiyi Guo, Duorong Yuan, Dong Xu, Guanghui Zhang, Suoying Sun, Fanging Meng and Minhua Jiang, *J Crystal Growth*, 2000, **40**, 75-79.
9.   Jiang X N, Yu D, Yuan D R, Lu M K, Guo S Y, Zhang G H and Duan X L, *Cryst ResTecnol.,* 2002, **37(1),** 67-75, *(Eng) Chem Abstr.,* 136, 22.348482t.
10.   Wang X Q, Xu D, Lu M K, Yuan D R, Huang J, Li S G, Lu G W and Liu H Y, *J Crystal Growth*, 2003, **3-4**, 432-437.
11.   Wang X Q, Xu M K, Lu D, Yuan D R, Xu S X, Guo S Y, Zhang G H and Liu J R, *J Crystal Growth,* 2001, **224(3-4),** 284-293, *(Eng) Elsevier Sci Chem Abstr.,* 2001, **135(6),** 84472.
12.   Shukla S N, Nigam H K, Upadhayay N, Khan S and Srivastava A, *Orient J Chem.,* 2005, **21(2)**, 277-282.
13.   Shukla S N, Nigam H K, Upadhayay N, Khan S and Srivastava A, *J Appl Biosci.,* 2006, **32(1)**, 68-73.
14.   Vogel A L, A Textbook of quantitative inorganic analysis; 4th Ed., (ELBS and Long Man Green London), 1978.
15.   Singh P P, Yadav S P and Sharma S B, *Aust J Chem.,* **1**977, **30**, 1921.
16.   Lever A B P, inorganic Electronic Spectroscopy, Elsevier, Newyork, 1955, 280.
17.   Biradar N S, Roddabasanagoudar V L and Aminabhavi T M, *Polyhedron*, 1984, **3(5)**, 575-580.
18.   Desmukh K K, Hundekar A M and Sen D N, *J Indian Chem Soc*., 1980, **57**, 1147.
19.   Pearson R G, *J Am Chem Soc*., 1963, **85,** 3533-3543; *Science,* 1966, **151,** 172-177.
20.   Klopmann G, *J Am Chem Soc*., 1968, **90**, 223-234.