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Metal complexes of Co(II), Cd(II) and Hg(II) with N, N,'-Bis (Benzylidene)-1,3, Phenylenediamine Schiff Base, Synthesis, Characterization and Antimicrobial studies

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Abstract

A new series of the bimetallic complexes of Co(II), Cd(II) and Hg(II) of 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 TEn□ of complexes have also been calculated to derive the binding side of the thiocyanate ligand .The spectral data shows that the Schiff base ligand is linked with comparatively harder metal Co^{2+} whereas SCN form bridge between the two metals. Magnetic susceptibility measurements indicate tetrahedral geometry around cobalt ion. The softness parameter suggest monomeric bridged structure for these complexes, newly synthesized bimetallic complexes have been screened 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 , Antimicrobial activity

Introduction

Schiff base are the condensation products of carbonyl compound (ketone or aldehyde) with primary amines, first invented by Hugo Schiff, which was named after him[1], these ligand are widely studied because of their coordinating properties and abilities [2] , due to special property of -C=N group (azomethine), Schiff bases are generally excellent chelating agents [3].

The importance of Schiff base complexes for bioinorganic chemistry, biomedical applications, supra molecular chemistry has been well recognized and reviewed [4], binding mode sensitivity of thiocyanate moiety has given rise to a rich and unique chemistry in recent years.

Schiff bases have been used as chelating ligand in coordination chemistry of transition metals, model system for biological macro molecules[5-6], they show biological activity including antibacterial, antifungal and herbicidal activity [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 activity of hetro - bimetallic complex of the fallowing type.

[MM'(SCN)4] → [(BENDAMB(1,3))M(NCS)$_2$M'(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 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[10].

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 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 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.

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.

Electronic spectra and Magnetic moments

The magnetic moment of the complexes containing Cobalt viz-1 and 2 ranges between 4.38 -4.85 BM. The Electronic spectra of these complexes show a band between 8047-8072cm^{-1} which can be assigned for the transition 4A$_2$(F)□4T$_1$(F) ($□_{□}$) and another band between 16,360-16554cm^{-1} may be attributed for the transition 4A$_2$(F)□4T$_1$(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 ion[13].10Dq values are in between 4983-4986cm^{-1} and □ parameter are between 0.66-0.69 suggesting quite good thermodynamic stability and good covalency in 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(1,3)Co(NCS)$_2$Cd(SCN)$_2$]	Dark brown	51	157^d	-	-	18.40 (18.64)	24.70 (24.89)
2	[BENDAMB(1,3)Co(NCS)$_2$Hg(SCN)$_2$]	Grey	58	160^d	7.38 (7.59)	25.68 (25.84)	16.40 (16.52)	-
3	[BENDAMB(1,3)Cd(NCS)$_2$Hg(SCN)$_2$]	Dirty white	58	149^d	13.30 (13.54)	23.89 (24.17)	15.30 (15.45)	-

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

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 2104-2170 cm^{-1} clearly indicates the presence of thiocyanate as bridging unit. Similarly the presence of two characteristic □(CN) bands for S-bonded terminal SCN Furthermore, the presence of bands in □(NCS), □(C-S), □(M-N) and □(M'-S) regions are diagnostic for the nature of thiocyanate bonding[12].

All the assignments are in favour of monomeric bridge structure for these complexes. 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 (□30-35cm^{-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(1,3) Co(NCS)$_2$Cd(SCN)$_2$]	2104(sh);2152(s) 2068(s);2092(w)	759(m);781(s) 720(sh)	471(w) 431(m)	1606(s)	304(m)	241(w)	M.B
2	[BENDAMB(1,3) Co(NCS)$_2$Hg(SCN)$_2$]	2112(sh);2170(s) 2066(s);2080(w)	761(m);772(s) 731(sh)	474(w) 417(m)	1600(s)	308(m)	240(w)	M.B
3	[BENDAMB(1,3) Cd(NCS)$_2$Hg(SCN)$_2$]	2107(sh);2168(s) 2081(s);2100(m)	751(m);789(s) 710(sh)	489(w) 416(m)	1603(s)	319(m	230(w)	M.B

^{1}H-NMR spectra

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

(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 δ8.69 in the complex **3** 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 Co^{2+}

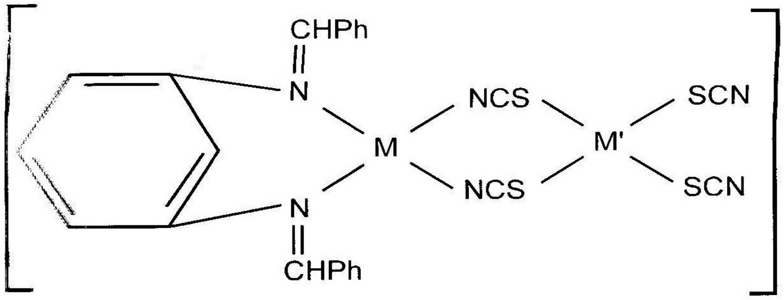
Table 3 - ^{1}H NMR data (scale ppm) of the complex

S.N	Complexes	Aromatic ring	-CH=N
1	[BENDAMB(1,3)Cd$(NCS)_2$Hg$(SCN)_2$]	7.11(s) 7.56(m)	8.69(s)

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

(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[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.



(A)

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[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 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

S.N	Complexes	TEn□ (M-M')	Nature of Bridge
1	[BENDAMB(1,3)Co$(NCS)_2$Cd$(SCN)_2$]	27.33	M.B
2	[BENDAMB(1,3)Co$(NCS)_2$Hg$(SCN)_2$]	23.51	M.B
3	[BENDAMB(1,3)Cd$(NCS)_2$Hg$(SCN)_2$]	23.56	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) Co$(NCS)_2$Cd$(SCN)_2$]	++	+
3	[(BENDAMB(1,3) Co$(NCS)_2$Hg$(SCN)_2$]	++	++
4	[(BENDAMB(1,3) Cd$(NCS)_2$Hg$(SCN)_2$]	+++	++

(-) 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)Co$(NCS)_2$Cd$(SCN)_2$]	69.7	73.3	45.4	93.7	74.2	55.2
2	[BENDAMB(1,3)Co$(NCS)_2$Hg$(SCN)_2$]	79.2	65.6	51.1	83.1	71.5	41.1
3	[BENDAMB(1,3)Cd$(NCS)_2$Hg$(SCN)_2$]	80.4	72.3	48.8	89.1	62.4	42.9

Conclusion

All newly synthesized hetro bimetallic complexes have monomeric bridged structure , in which SCN forms bridge between two metals. All the complexes shows good microbial activity against bacteria and fungi, need further screening at lower dilution.

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References :

[1]. F.R. Hartley, C.J. Burgess, & R.Al Cook, In solution equilibrium,New York 1980
[2]. R.V.Singh, N.Fahmi,& M.K. Biyala, J.Chem.Sic iran 2005 2, 40
[3]. H. Singh, S.N.Shukla,& R.S.Srivastava, Bull.Soc.chim.Fri, 1991 128:530-536
[4]. L. Hunter, & J. A. Marriott, J Chem Soc., 2000, 1937
[5]. M.K.Taylor, K.D.Troter, J.Reglinski, A.R. Kenndy, C.M.Spickett, & R.S. Sowder, Inorg chim Acta 2008, 361 2851-2862
[6]. D. Sandhanamalar, S. Vedanayaki, & R. Rajavel, Chem Sc. Trans 2013 2(2) 529-5377
[7]. M.Abou, & H. Farook, J.Iran Chem.Soc 2008 5(1), 122-134

[8]. S.N. Shukla, H.K Nigam, N. Upadhayay, S. Khan & A. Srivastava, J. Appl Biosci. June 2006 32(1) 68-73
[9]. N. Upadhayay, W.J.P.R, 2016, 5(4),1034-1041
[10]. A.L. Bogel, A Text Book of quantitative inorganic Analysis , 3rd End(ELBS and Long Man Green London) 1964 526
[11]. D.H. Burch, Record Chem. Progr. 1964 25, 107
[12]. P.P Singh, S. P. Yadav, S.B. Sharma Aust.J.chem 1977 30,1921
[13]. Lever A.B.P., inorganic Electronic spectroscopy ; Elsevier,Newyork 1955 p 280
[14]. N.S.Biradar, Roddabasanagoudar ; T.M. Aminabhavi, polyhedron1984 3,575
[15]. K.K. Desmukh, A.M. Hundekar, D.N. Sen, J.indian chem..Soc 1980 57,1147
[16]. R.G. Pearson; J.Am.chem.soc 1965 85 3533 science 151
[17]. G. Klopmann; J.Am.chem.soc. 1968 90, 223
[18]. B. G. Tweedy Phytopathology, 1964, 55, 910-914