

Studies on Reactivity of Homo and Heterobimetallic Thiocyanate Bridged Lewis Acid with Schiff Base Derived from 1,2-Diaminopropane with Salicylaldehyde

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New complexes of $MM'(SCN)_4$ ($M = Co^{2+}, Ni^{2+}, M' = Cd^{2+}, Hg^{2+}$) with Schiff base derived from 1,2-diaminopropane with salicylaldehyde, have been synthesized and characterized by elemental analyses, molar conductance, magnetic moment, FTIR, electronic and 1H -NMR spectral studies. The softness parameters, ΔTE_n^s of complexes have also been calculated to derive the probable structures. The complexes have also been investigated for insecticidal activity against red cotton bug (*Dysdercus koenigii*).

Key Words:

INTRODUCTION

The binding mode sensitivity of thiocyanate moiety has given rise to a rich and unique chemistry in recent years¹⁻⁵. The nature of both metal and ligand plays an important role to decide the nature of bridge and environment around a metal ion. Very recently, bimetallic thiocyanate complexes like $CdHg(SCN)_4$ and $MnHg(SCN)_4$ have given a new dimension to the synthesis and study of potentially useful second harmonic generation (SHG) organometallic non-linear optical crystals⁶⁻⁸.

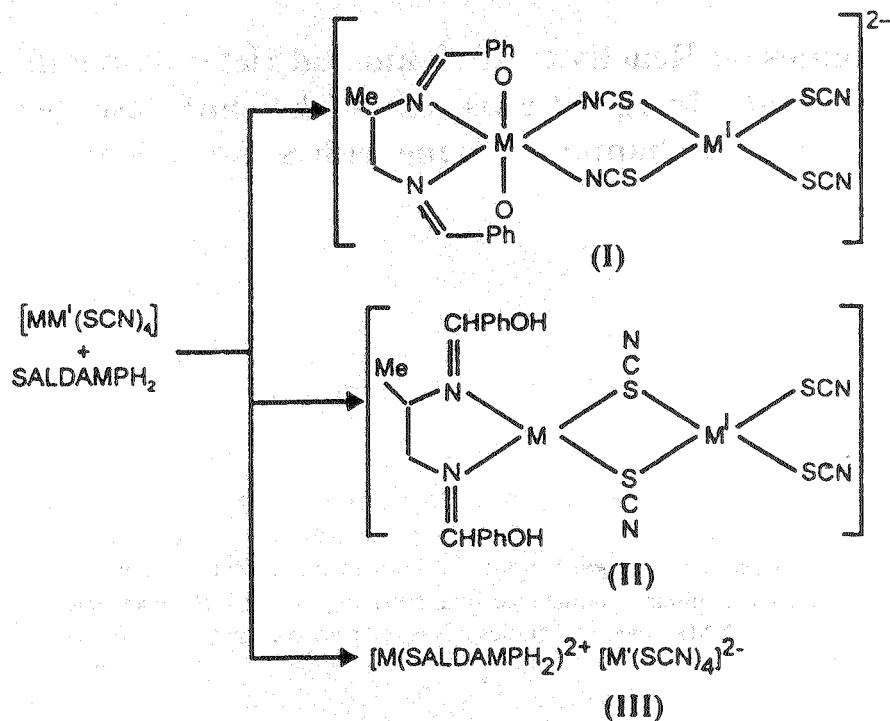
Schiff base ligands and its metal chelates have been paid high attention during the past years, due to their varied range of activity⁹⁻¹². Recently, Schiff base chelates are reported to have antineoplastic activity¹³. Literature survey reveals that reactions of bimetallic Lewis acid with Schiff base have not been studied so far. Therefore, it will be of interest to see the reaction of bimetallic Lewis acid and Schiff base in 1 : 1 molar ratio.

The result suggested that complex (I) was only formed in each case, except

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SALDAMPH₂ = N,N' - bis (salicylidene) - 1,2 - diaminopropane

in homobimetallic mercury complex, where experimental results are in favour of complex (II). Furthermore, we also thought that the above complexes obtained after coupling of biologically active Schiff base and bimetallic Lewis acid may prove to possess more biological activity.

Thus, we are of the view that such a study would be more illuminating in terms of structural assignments, chemical reactivities and biological activity of the complexes formed.

EXPERIMENTAL

Solvents were dried and distilled in the usual manner. Cobalt(II), nickel(II), cadmium(II) and mercury(II) nitrates (all BDH) were used as received without further purification. Potassium thiocyanate (Sarabhai M. Chemicals) was used after drying in vacuum. 1,2-Diaminopropane (Lancaster, UK) and salicylaldehyde (CDH) was used as received. FTIR spectra were measured on a Biored-135 FTS using KBr pellets. The details of analyses and physical measurements were almost same as described earlier².

Preparation of Schiff Base

Schiff base ligand (N,N'-bis(salicylidene)-1,2-diaminopropane (SALDAMPH₂)) was prepared by refluxing 1,2-diaminopropane with salicylaldehyde in 1 : 2 molar ratio, for 8–10 h in ethanol. Concentrated ethanolic solution was poured into ice-cooled water along with constant stirring which yielded a viscous mass. It was recrystallized to obtain a light brown solid which gave satisfactory C, H, N, IR and ¹H NMR data.

Preparation of Complexes

Metal dithiocyanates (metal = Co, Ni, Cd, Hg) were prepared following literature procedure¹⁴. For the preparation of Lewis acid $MM'(SCN)_4$, solution of $M(NCS)_2$ and $M'(SCN)_2$ were mixed in 1 : 1 molar ratio and stirred for 1 h. To the solution or suspension of the above Lewis acid, ethanolic solution of Schiff base ligand (SALDAMPH₂) was added in 1 : 1 molar ratio and stirred for 20–24 h. To the above solution, dil. NaOH solution was added dropwise; solid separated in each case was filtered and washed with ethanol, dried *in vacuo* and recrystallized from chloroform/acetone mixture. All complexes are partially/completely soluble in DMSO.

A slightly different method was employed for the preparation of homobimetallic mercury complex. To a solution of $Hg(SCN)_2$ in ethanol, an ethanolic solution of Schiff base ligand was added in 1 : 1 molar ratio and stirred for 1 h and then 1 mol of ethanolic solution of $Hg(SCN)_2$ was added to the above solution and stirred for 24 h. A dirty white solid was filtered off, washed with ethanol and dried *in vacuo* and recrystallized from chloroform/acetone mixture.

RESULTS AND DISCUSSION

The stoichiometries of the complexes are in agreement with elemental analyses given in Table-1. All the complexes show conductance in the range 50–75 mho.cm²/mol indicating 1 : 2 electrolytic nature of the complex, except complex 6 which displays very low conductance (*ca.* 25 mho.cm²/mol).

TABLE-1
ELEMENTAL ANALYSES, COLOUR, YIELD AND MELTING POINTS OF THE COMPLEXES

Complexes (Colour)	Yield (%)	m.p. (°C)	Elemental analyses			
			M (Co/Ni/ Cd)	M' (Cd/Hg)	S	(Co + Cd)
[(SALDAMP)(Co(NCS) ₂ Cd(SCN) ₂)]Na ₂ (Reddish brown)	50	256 ^d	—	—	17.36 (17.50)	23.30 (23.42)
[(SALDAMP)Co(NCS) ₂ Hg(SCN) ₂]]Na ₂ (Brown)	65	225 ^d	7.01 (7.19)	24.22 (24.47)	15.42 (15.62)	—
[(SALDAMP)Ni(NCS) ₂ Cd(SCN) ₂]]Na ₂ (Yellow green)	52	215 ^d	7.86 (8.03)	15.21 (15.37)	17.40 (17.50)	—
[(SALDAMP)Ni(NCS) ₂ Hg(SCN) ₂]]Na ₂ (Yellow)	48	262 ^d	7.02 (7.16)	24.26 (24.48)	15.15 (15.62)	—
[(SALDAMP)Cd(NCS) ₂ Hg(SCN) ₂]]Na ₂ (Dirty white)	65	220 ^d	12.56 (12.86)	22.80 (22.97)	14.56 (14.66)	—
(SALDAMPH ₂)Hg(NCS) ₂ Hg(SCN) ₂ (Dirty white)	60	185	—	43.60 (43.83)	13.72 (13.98)	—

Satisfactory C, H and N analyses have been obtained for all complexes; d: decomposed

IR Spectra

The infrared spectra of all the complexes show the presence of four bands in —CN stretching region. The presence of two bands in between 2170–2110 cm^{-1} clearly indicates the presence of bridged thiocyanate unit. Similarly, the presence of two characteristic $\nu(\text{CN})$ bands for S-bonded terminal SCN in between 2090–2068 cm^{-1} indicates the presence of S-bonded SCN. In addition to this, the presence of bands in $\delta(\text{NCS})$, $\nu(\text{C—S})$, $\nu(\text{M—N})$ and $\nu(\text{M'—S})$ regions is diagnostic for the nature of thiocyanate bonding¹⁴. These all assignments are clear evidence in support of monomeric bridged structure.

A strong band at 1630 cm^{-1} in Schiff base is characteristic of azomethine ($>\text{C}=\text{N}$) group^{15, 16}. In all complexes, this band is shifted towards the lower frequency region (35–25 cm^{-1}), indicating coordination of the Schiff base azomethine nitrogen atoms.

The complexes from 1–5 show no bands assignable to phenolic $\nu(\text{OH})$, but the band 1250 cm^{-1} in Schiff base due to $\nu(\text{C—O})$ is shifted towards higher frequencies. Similarly, a new band arising in between 418–405 cm^{-1} is assigned for $\nu(\text{M—O})$. These two evidences suggest the bonding from oxygen atom to metal.

All the IR assignments are in favour of monomeric bridged structure I, except in complex 6, *viz.*, homobimetallic mercury complex, where the presence of a band assignable to phenolic $\nu(\text{OH})$ and absence of $\nu(\text{M—O})$ confirms the devoid of M—O bonding in the complex, suggesting the structure II for homobimetallic mercury complex (Table-2).

Electronic Spectra

Magnetic moments of all the complexes containing cobalt, *viz.*, 1 and 2 are 5.1 and 4.9 BM, respectively. The electronic spectra of these complexes show a broad band in between 10,100–9,500 cm^{-1} , assigned for ${}^4\text{T}_{1g} \rightarrow {}^4\text{T}_2(\text{F})$ (ν_1) and another band between 22,200–21,750 cm^{-1} , assigned for ${}^4\text{T}_{1g} \rightarrow {}^4\text{T}_{1g}(\text{P})$ (ν_3). However, ν_2 band assigned for transition ${}^4\text{T}_{1g} \rightarrow {}^4\text{A}_{2g}(\text{F})$ was not observed, probably being formally a two electron transition. Two other bands observed on higher wavenumber side are due to charge transfer. All these assignments suggest octahedral environment around cobalt(II) ion¹⁷.

Magnetic moments of the complexes containing nickel, *viz.*, 3 and 4, are 3.00 and 3.10 BM, respectively. The electronic spectra of these complexes show three bands: the first band in between 10,700–9,040 cm^{-1} , assigned for ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{2g}(\text{F})$ (ν_1), the second band in between 15,500–14,900 cm^{-1} , assigned for ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{F})$ (ν_2) and the third band in between 26,880–24,389 cm^{-1} , assigned for ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{P})$ (ν_3). A band between 33,700–32,670 cm^{-1} is a charge transfer band. All these suggest octahedral environment around nickel(II) ion¹⁷.

In complexes 5 and 6, the octahedral environment around Cd(II) ion and tetrahedral environment around Hg(II) ion is observed. All the spectral bands, magnetic moments and assignments along with ligand field parameters are listed in Table-3.

¹H NMR Spectra

¹H NMR signals of compounds 5 and 6 along with ligand are given in Table-4. The following conclusions can be derived by comparing the spectra of ligand and their corresponding complexes.

TABLE-2
 INFRARED SPECTRAL DATA (cm^{-1}) OF THE COMPLEXES

S. No.	Complexes	$\nu(\text{C}-\text{N})$	$\nu(\text{C}-\text{S})$	δNCS (bend)	$>\text{C}=\text{N}$ (str) azomethine	$\nu(\text{M}-\text{N})$	$\nu(\text{M}'-\text{S})$	$\nu(\text{M}-\text{O})$	$\nu(\text{C}-\text{O})$
1.	$[(\text{SALDAMP})\text{Co}(\text{NCS})_2\text{Cd}(\text{SCN})_2]\text{Na}_2$	2120 (sh); 2170 (s) 2070 (s); 2090 (w)	794 (m); 826 (w)	480 (m)	1590 (s)	300 (m)	230 (w)	411 (w)	1278 (m)
2.	$[(\text{SALDAMP})\text{Co}(\text{NCS})_2\text{Hg}(\text{SCN})_2]\text{Na}_2$	2116 (sh); 2165 (s); 2075 (s); 2088 (w)	785 (m); 831 (w); 750 (m)	475 (m)	1595 (s)	305 (w)	235 (w)	405 (w)	1282 (m)
3.	$[(\text{SALDAMP})\text{Ni}(\text{NCS})_2\text{Cd}(\text{SCN})_2]\text{Na}_2$	2110 (sh); 2139 (s); 2073 (s); 2090 (sh)	795 (m); 826 (w); 740 (m)	485 (m)	1605 (s)	309 (m)	240 (w)	415 (m)	1268 (m)
4.	$[(\text{SALDAMP})\text{Ni}(\text{NCS})_2\text{Hg}(\text{SCN})_2]\text{Na}_2$	2111 (sh); 2148 (s); 2071 (s); 2086 (sh)	788 (m); 805 (w); 743 (w)	478 (m)	1582 (s)	310 (m)	228 (w)	418 (m)	1280 (m)
5.	$[(\text{SALDAMP})\text{Cd}(\text{NCS})_2\text{Hg}(\text{SCN})_2]\text{Na}_2$	2118 (sh); 2153 (s); 2068 (s); 2085 (sh)	786 (m); 740 (w)	469 (w)	1598 (s)	315 (m)	234 (w)	408 (w)	1285 (m)
6.	$(\text{SALDAMP})_2\text{Hg}(\text{NCS})_2\text{Hg}(\text{SCN})_2$	2112 (w); 2150 (sh); 2070 (w); 2000 (s)	780 (m); 749 (m)	460 (m); 480 (m)	1600 (s)	288 (w)	240 (m)	---	1250 (m)

TABLE-3
ELECTRONIC SPECTRAL DATA (cm^{-1}) FOR THE COMPLEXES

S.No.	Complexes	μ_{eff}	Bands observed (cm^{-1})	Assignments	Spectral parameter		
					Dq (cm^{-1})	B	β
1.	[(SALDAMP)Co(NCS) ₂ Cd(SCN) ₂]Na ₂	5.10	9500	$^4T_{1g} \rightarrow ^4T_{2g}(F) (v_1)$	1000	910	0.90
			2200	$^4T_{1g} \rightarrow ^4T_{1g}(P) (v_3)$			
			39283	Charge transfer			
			40800	Charge transfer			
2.	[(SALDAMP)Co(NCS) ₂ Hg(SCN) ₂]Na ₂	4.90	10,100	$^4T_{1g} \rightarrow ^4T_{2g}(F) (v_1)$	1050	932	0.91
			21,750	$^4T_{1g} \rightarrow ^4T_{1g}(P) (v_3)$			
			37,800	Charge transfer			
			39,980	Charge transfer			
3.	[(SALDAMP)Ni(NCS) ₂ Cd(SCN) ₂]Na ₂	3.00	10,700	$^3A_{2g} \rightarrow ^3T_{2g}(F) (v_1)$	1070	720	0.69
			15,500	$^3A_{2g} \rightarrow ^3T_{1g}(F) (v_2)$			
			26,880	$^3A_{2g} \rightarrow ^3T_{1g}(P) (v_3)$			
			33,700	Charge transfer			
4.	[(SALDAMP)Ni(NCS) ₂ Hg(SCN) ₂]Na ₂	3.10	9040	$^3A_{2g} \rightarrow ^3T_{2g}(F) (v_1)$	1080	754	0.71
			14,900	$^3A_{2g} \rightarrow ^3T_{1g}(F) (v_2)$			
			24,389	$^3A_{2g} \rightarrow ^3T_{1g}(P) (v_3)$			
			32,670	Charge transfer			
5.	[(SALDAMP)Cd(NCS) ₂ Hg(SCN) ₂]Na ₂	diamag	36,400	Charge transfer	—	—	—
			40,680	Charge transfer			
6.	(SALDAMP) ₂ Hg(NCS) ₂ Hg(SCN) ₂	diamag	42,640	Charge transfer	—	—	—

- (i) A signal due to —OH of salicylate group at δ 9.6 observed in ligand is absent in complex 5, but present in complex 6.
- (ii) The proton signal due to CH=N group appearing at δ 8.3 in the Schiff base is shifted to downfield in both the complexes, probably due to lone pair donation by the azomethine nitrogen to the metal.
- (iii) The proton signal for —CH₃, —CH₂— and —CH appears at proper place in ¹H NMR spectra.

Therefore, on the basis of IR, electronic spectra and ¹H NMR spectra, monomeric bridged structure (A) for the complexes 1, 2, 3, 4, 5 and structure (B) for the complex 6 is suggested. In both the structures, SCN form bridge between the two metals, but in structure (A) Schiff base is linked through azomethine nitrogen and phenolic oxygen to the metal M; however, in structure (B), Schiff base is linked through azomethine N only, probably due to more favourable tetrahedral geometry around mercury(II) ion. This will also be supported by the lower conductance value of complex 6.

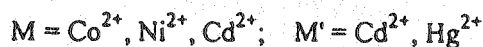
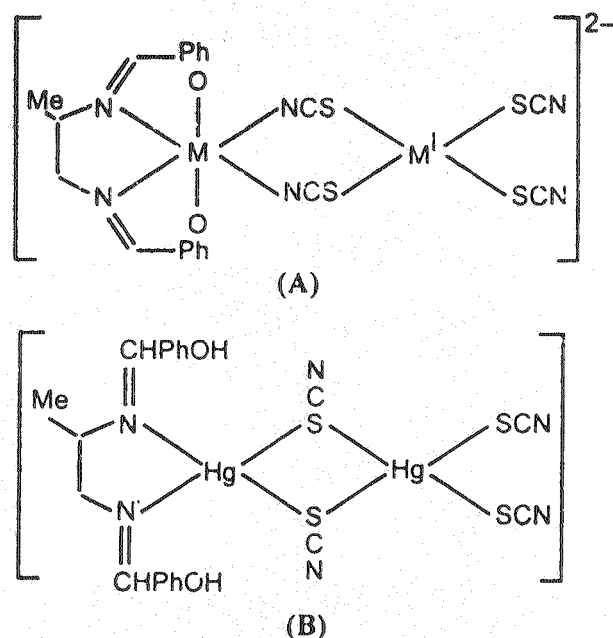


Fig. 1.

TABLE-4
¹H NMR DATA (δ SCALE, ppm)

Complexes	Aromatic ring	—CH=N	—CH ₃	—CH ₂	—CH	—OH
SALDAMPH ₂	7.15 (s) 7.50 (m)	8.30 (s)	2.10 (d)	3.20 (d)	4.85 (t)	9.6 (s)
[(SALDAMP)Cd(NCS) ₂ Hg(SCN) ₂] ₂ Na ₂	7.10 (s) 7.60 (m)	8.60 (s)	2.15 (d)	3.24 (d)	4.80 (t)	—
(SALDAMPH ₂)Hg(NCS) ₂ Hg(SCN) ₂	7.15 (s) 7.55 (m)	8.55 (s)	2.08 (d)	3.26 (d)	4.60 (t)	9.62 (s)

TABLE-5
CALCULATED VALUES OF TOTAL SOFTNESS PARAMETERS

S. No.	Complexes	$\Delta TE_n^{\#}(M - M')$	Nature of bridge
1.	$[(SALDAMP)Co(NCS)_2Cd(SCN)_2]Na_2$	36.35	MB
2.	$[(SALDAMP)Co(NCS)_2Hg(SCN)_2]Na_2$	33.76	MB
3.	$[(SALDAMP)Ni(NCS)_2Cd(SCN)_2]Na_2$	36.29	MB
4.	$[(SALDAMP)Ni(NCS)_2Hg(SCN)_2]Na_2$	33.70	MB
5.	$[(SALDAMP)Cd(NCS)_2Hg(SCN)_2]Na_2$	35.81	MB
6.	$(SALDAMP)_2Hg(NCS)_2Hg(SCN)_2$	23.00	MB

MB: Monomeric bridged

Structure (A) for the complexes 1, 2, 3, 4 and 5 is also supported on the following grounds:

- (i) The higher 10 Dq values for the complexes 1, 2, 3 and 4 indicate the presence of bridged NCS group.
- (ii) HSAB theory also supports the binding of thiocyanate ion in the metal complexes. Nitrogen of thiocyanate ion being the hard centre will link comparatively harder metal ions and nickel, whereas the sulphur end of the thiocyanate ion will link to soft cadmium and mercury metal ions.

Application of softness parameter to the nature of bridge

The nature of cationic-anionic, polymeric bridged and monomeric bridged complexes was related with difference in quantitative values of softness of M and M'. These values were derived by adopting quantum mechanical procedure given by Klopman¹⁹.

The total softness values of M and M' have been derived by adding the softness values of ligands to the reported values of M and M'. The $\Delta TE_n^{\#}(M - M')$ values and predictions obtained from them are presented in Table-5, since the calculated values of $\Delta TE_n^{\#}(M - M')$ of all the complexes range between 23.00–36.35, which can be accounted well for monomeric bridged structure²⁰.

Insecticidal experiments

0.1% solution (in DMSO) of complex 6 was tested for insecticidal activity against red cotton bug (*Dysdercus koenigii*) by contact poison technique. A graph was plotted between percentage mortality and the time recorded (Fig. 2). It can be observed from the graphs synergic effects of complex and solvent have greater lethality than the effect of the Schiff base ligand and the solvent. This is probably due to the 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.

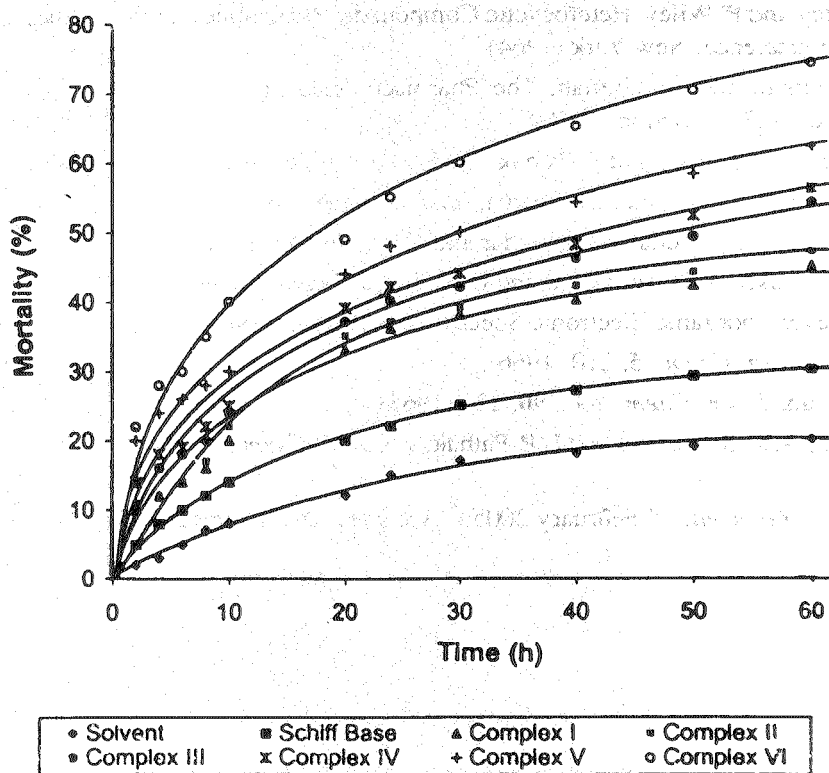


Fig. 2

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