

Original Research Article

Studies of Complexes of Para Bromo Phenyl mercury Thiocyanates with M^I (BIS Salicylidene 1:2 propane diamine)

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ABSTRACT

The Lewis base character of organomercury thiocyanates has been explored and few organometallic compounds we have study. Here we report the preparation and study of organometallic compound of general formula $(RHgSCN)_2 M(NCS)_2$ [R=P-Bromophenyl: M= Co (II), Ni(II), Cu(II), Zn(II), Mn (II)]. The complexes have been synthesized by reacting $RHgSCN$ with $M(NCS)_2$. These compounds also act as Lewis acids on account of unsaturation at M and at Hg. Due to this unsaturation they have been reacted with M^I (Salpn) [M^I = Co(II), Ni(II), Cu(II), Zn(II), Salpn = $(C_{17}H_{16}N_2O_2)$]. Structure of these complexes has been established on the basis of different physico-chemical methods.

KEYWORDS

Mercury | Bromo Phenyl | Salicylidene | Organomercury | Thiocyanates

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Introduction

There has been considerable interest in the coordination chemistry of transition metal involving nitrogen & oxygen donors ligands due to increasing recognition of the role of this metal in biological system. These complexes are significant not only for their redox-active role in several biochemical processes but also for the diversity in their magnetic behavior. Manganese complexes containing tetra co-ordinating ONNO donor ligands are well studied as the structural models of active site of many in Metallo enzymes. The most important operation showed by Mn in Nature is the Photolytic Oxidation of water of Dioxygen in the oxygen evolving complex (OEC) of photo system – II (PS II) found in the photo synthetic apparatus of green plants and certain cyanobacteria.

The chemistry of carbonylhydrazone compound has been studied by Swamy & Siddalingaiah. Variety of metal complexes of symmetrical dihydrazones derived from thiocarbonylhydrazides have been synthesized and their stereo chemistry is also reported. Hydrazones and their complexes with transition metals have provoked wide interest for their apparent biological and pharmaceutical activities. Some carbonylhydrazone ligands behave as N, N- chelating agent in the Neutral form and an ONNO(NNO-Chelating agent in deprotonated form, Warad *et al.* have synthesized and characterized the carbonylhydrazone bis (salicylaldehyde) ligand and its transition metal complexes. They proposed that this ligand act as a dinegative tetradentate (N_2O_2) ligand in forming a tetrahedral complexes. Complexes of carbonylhydrazone with non transition metal ion such as organotin (IV) have not received much attention. Affan *et al.* have reported a new series of di organotin (IV) complexes by the reaction of $R_2 Sn Cl_2$ ($R = Me, Bu, Ph$) with O, N, O – tridentate carbonylhydrazone ligand derived from carbonylhydrazone. The structure have been established on the basis of IR & X-ray Studies.

Experimental

Reagent grade solvents were purified and dried before use para bromo aniline was used from

fresh bottles. Para bromo phenyl mercury chloride was prepared by diazotization method ⁽¹⁻³⁾ as discussed below:

Preparation of Para Bromo Phenyl Chloride (P-BrC₆H₄HgCl): 17.2 gms (0.1 mole) of P-bromo aniline was added to a mixture of 50 ml of concentrated hydrochloric acid and 50 ml of water. The mixture was cooled by adding ice and stirred vigorously. The temperature of the reaction was maintained between 0 to 5°C and solid sodium nitrite (7.0 g, 0.1 mole) was added in small fractions. After stirring for about half an hour, the whole mass was filtered. To the clear filtrate a cooled solution of (27.0 g, 0.1 mole) mercuric chloride in 30 ml of concentrated hydrochloric acid was slowly added with vigorous stirring. The stirring was continued for 15 minutes more and the precipitate was filtered, washed with water, followed by ether and dried in air. The pBrC₆H₄N₂HgCl so obtained was mixed with 12 gram of copper powder in 100 ml of cold water in fraction with stirring. The mixture was stirred for one hour and allowed to stand overnight and filtered. The residue was extracted with ethylene, which on cooling gave white crystals of P-BrC₆H₄HgCl.

Preparation of Para Bromo Phenyl Mercury Thiocyanate P-BrC₆H₄HgSCN:

Para bromo phenyl Mercury chloride was converted into its thiocyanate derivative by reacting with potassium thiocyanate in 1:1 molar ratio in acetone. The potassium bromide was filtered off and the filtrate was concentrated by vacuum evaporation on addition of water to the concentrate solution, p-bromo phenyl mercury thiocyanate separated, which was followed by ether and dried in air. The compound was recrystallized from acetone. The purity of the thiocyanate derivative was tested by elemental analysis and infra-red spectral measurement. p-BrC₆H₄HgSCN. m.p. 195°C Found Nitrogen 3.30%, Sulphur 7.60%, Mercury 48.20% Calculated Nitrogen 3.37%, Sulphur 7.71%, Mercury 48.38% Infra-red spectral band position. ν (C-N) 2180 cm^{-1} , ν (C-S) 765 cm^{-1} , δ (NCS) 440 cm^{-1} .

Preparation of Lewis Acid [(p-BrC₆H₄HgCN)₂ M(NCS)₂]: [M=Co(II), Ni(II), Cu(II), Zn(II), Mn(II)] 1 mole of metal thiocyanate prepared from their respective metal nitrates by the reaction of potassium thiocyanate, was suspended in acetone and was reacted with 2 m mole of p-BrC₆H₄HgSCN in the same solvent. The mixture was stirred first for two hours and then refluxed for twelve hours. The compound thus formed was filtered, washed with the ether, acetone and dried in vacuum.

The Lewis acid of cobalt and nickel were also prepared by heating their corresponding pyridine complexes (p-BrC₆H₄HgSCN)₂Co(NCS)₂ (Py)₂ and (p-BrC₆H₄HgCN)₂ Ni(NCS)₂ Py₂ to get a good yield of the Lewis acids.

Preparations of M^I (Salpn): [M^I = Co(II), Ni(II), Cu(II), Zn(II), Salpn = (C₁₇H₁₆N₂O₂)]: 5.76 gm of salicylaldehyde was dissolved in 65 ml of 95% ethanol. 2.03 gm of 1:2-propane diamine was also dissolved in the same volume of ethanol. This solution was slowly added to the solution of salicylaldehyde with continuous stirring on an ice bath. The schiff's base precipitated which was dissolved by heating to 60°C, 5.76 gm of cobalt acetate tetrahydrate was dissolved in 30 ml of water and heated to 60°C the Cobaltous acetate solution was rapidly poured into the alcoholic solution of the schiff's base and well shaken. A brown gelatinous product was formed which rapidly changed into large red crystals. M^I(Salpn): [M^I = Co(II), Ni(II), Cu(II), Zn(II), were similarly prepared by using their respective hydrated metal acetates in place of cobalt analogue. These schiff's base complexes were referred to as M^I(Salpn) and used as ligands.

Preparation of Trimetalic Complexes [(RHgSCN)₂ M(NCS)₂ M^I(Salpn)] M = Co(II), Ni(II), Cu(II), Zn(II), Mn(II): =M^I = Co(II), Ni(II), Cu(II), Zn(II); R = p-BrC₆H₄ - salpn = (C₁₇H₁₆N₂O₂) 0.1 mole of (RHgSCN)₂M(NCS)₂ [R=p-bromo phenyl] and 1 mole of M^I (salpn) were separately dissolved in 100 ml of methanol or acetone, both the solutions were mixed and stirred for about 72 hours. The solid compound separated, which was filtered, washed with acetone and recrystallized from DMSO and dried in vacuum.

Analysis of the complexes

The complexes were analyzed for cobalt as anthranilate, nickel as dimethyl glyoximate, mercury as sulphide and zinc as zinc ammonium phosphate, sulphur was estimated as barium sulphate and nitrogen by semi-micro kjeldahls method. Analytical results along with M.Ps are presented in table 1-2.

Physical Measurements

The molar conductance of the complex were measured in dimethylsulphoxide (DMSO) using a Philips conductivity bridge model PR-9500. The magnetic susceptibility measurements were made at room temperature by

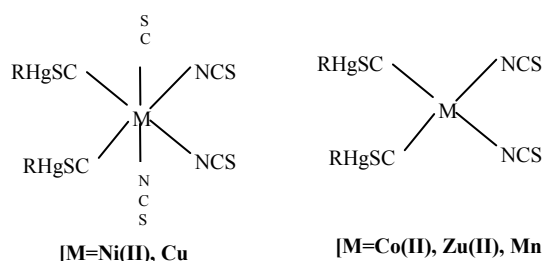
Gouy's method using HgCo(SCN)₄ as standard. The infra red spectral measurements were made on Pye Unicam SP-3-300 spectrophotometer in the range 4000 cm⁻¹ -200 cm⁻¹ and the electronic spectrophotometer.

Results and Discussion

Since Lewis acids "(RHgSCN)₂ M(NCS)₂" have unsaturation at M they been reacted with M^I (salpn) and the adducts of general formula (RHgSCN)₂ M(NCS)₂ M^I (Co(II), Ni(II), Cu(II), Zn(II), Mn(II): =M^I = Co(II), Ni(II), Cu(II), Zn(II); salpn = (C₁₇H₁₆N₂O₂); R=p-Bromo phenyl] was obtained. The structure of these complexes has been established with the help of various physico-chemical studies. The discussion is presented under the following heads:

Lewis Acids

On reaction with M(NCS)₂ the RHgSCN form the complex of general formula formula (RHgSCN)₂ M(NCS)₂ [M =(Co(II), Ni(II), Cu(II), Zn(II), Mn(II); R=p-Bromo phenyl] which have been referred to as Lewis acids. Various studies (⁴⁻⁶) reveal that cobalt, zinc and manganese have tetrahedral geometry in the Lewis acids (fig. 1). In case of nickel and copper Lewis acids the geometry is octahedral due to axial coordination of thiocyanate groups of other molecules of adjacent layers fig. 1



The complex formed are non conducting in dimethylsulphoxide (DMSO). There is no significant change in molar conductance values of various complexes. Molecular weights of the complexes, determined by cryoscopic method, indicate that they are monomeric in nature (Table 3-4). On comparison of various infra-red spectral bands of RHgSCN and $\text{M}^{\text{I}}(\text{salpn})$ with the corresponding bands in $(\text{p-BrC}_6\text{H}_4\text{HgSCN})_2\text{M}(\text{NCS})_2$ $\text{M}^{\text{I}}(\text{salpn})$ changes are observed in $\nu(\text{C-N})$, $\nu(\text{C-S})$ and $\nu(\text{C-O})$ table-5. The $\nu(\text{C-N})$ and $\nu(\text{C-S})$ bands in all these cases show positive shifts. The position of these bands indicates that the thiocyanate of RHgSCN becomes bridging probably by coordination to M through its nitrogen end ⁽⁸⁻¹⁰⁾.

The bands observed at about 2090 cm^{-1} can be assigned to N-bonded terminal thiocyanate arising from $\nu(\text{M-NCS})$.

A change in the phenolic stretchings mode in the $1500\text{-}1600\text{ cm}^{-1}$ region be used to indicate coordination through the oxygen of $\text{M}^{\text{I}}(\text{salpn})$. A comparison of IR spectra of $\text{M}^{\text{I}}(\text{salpn})$ with the spectra of adducts show that there is a positive shift in the bands assigned to phenolic C-O stretching (table 6-7) and coordination of $\text{M}^{\text{I}}(\text{salpn})$ through the oxygen atom to M of $(\text{RHgSCN})_2\text{M}(\text{NCS})_2$. The other possible site of coordination is the imino group of $\text{M}^{\text{I}}(\text{salpn})$. The bands at 1380 cm^{-1} and 1340 cm^{-1} assigned to the imino group remain unaltered. The position of IR bands diagnostic of thiocyanate regions have also been examined, to see the effect of coordination through the oxygen ⁽¹¹⁻¹⁴⁾ atom of M (salpn) to M of $(\text{RHgSCN})_2\text{M}(\text{NCS})_2$. The coordination of $\text{M}^{\text{I}}(\text{salpn})$ will change the geometry of Co(II), Mn(II) and Zn(II) from tetrahedral in the Lewis acids to octahedral in the adducts. The change will effect the position of IR spectral bands and also the electronic spectral parameter. The position of the $d(\text{M-NCS})$ bands where M is Co(II), Zn(II) and Mn(II) is changed from $280\text{-}325\text{ cm}^{-1}$ to $230\text{-}299\text{ cm}^{-1}$. This negative shift is on account of a change in the tetrahedral geometry around M in the Lewis acids to octahedral in the adducts. Such a change is not observed when M in Ni(II) or Cu(II), because ge-

ometry around M remains octahedral both in the Lewis acids and the adducts.⁽¹⁵⁻¹⁷⁾ The IR spectra of adducts (Table 6-7) show that there is no significant change in the position of the $\nu(\text{C-N})$, $\nu(\text{C-S})$ and $d(\text{NCS})$ bands. This shows that the bridging nature of thiocyanate in the Lewis acids is retained in the adducts.⁽¹⁸⁻²¹⁾

Bailey *et al.*⁽²²⁾ have relied more on $\nu(\text{C-S})$ bands for determining the nature of bonding in thiocyanate ions. The position shift in $\nu(\text{C-S})$ band on complex formation has been designated as $\nu(\text{C-S})$. The $\nu(\text{C-S})$ values have been used for deriving the comparative donor strength of various RHgSCN and for comparative acceptor strength of various M. For the former the $\nu(\text{C-S})$ values have been derived by changing the R for a particular M and for the latter the M has been varied for a particular R. The RHgSCN has been considered as donor towards $\text{M}(\text{NCS})_2\text{M}^{\text{I}}(\text{salpn})$. The $\nu(\text{C-S})$ values derived by change of M, indicate the following order of acceptor strength of various M in $(\text{RHgSCN})_2\text{M}(\text{NCS})_2$ [M=Co(II), Ni(II), Cu(II), Zn(II)]. The values are higher when M is Ni(II) and lowest when M is Zn(II). The sequence is as follows : Ni(II) > Co(II) > Mn(II) > Zn(II)

The order is consistent with the established order ⁽²³⁾. The electronic spectra of $(\text{RHgSCN})_2\text{Ni}(\text{NCS})_2$, $\text{M}^{\text{I}}(\text{salpn})$ also show the presence of three bands at $24240\text{-}26320\text{ cm}^{-1}$ $16130\text{-}16380\text{ cm}^{-1}$ and $9990\text{-}10640\text{ cm}^{-1}$, which are assigned to ${}^3\text{A}_{2g} \otimes {}^3\text{A}_{2g}(\text{P}) \nu_3$, ${}^3\text{T}_{2g} \otimes {}^3\text{T}_{1g}(\text{F}) \nu_2$ and ${}^3\text{A}_{2g} \otimes {}^3\text{T}_{2g}(\text{F}) \nu_1$, transition respectively values spectral parameters Dq , B^{I} and b have been derived with the help of ν_2 and ν_3 bands and are include in table 9.

The spectral band position parameters and magnetic moment values indicate octahedral coordination geometry around cobalt and nickel in the complexes, it can be presumed that they [Zn(II), Mn(II), Cu(II)] too have octahedral geometry around them. On the basis of above studies octahedral structure as given in fig. 2 can be proposed to the complexes^(25,26). ADDUCTS: $[\text{RhgSCN})_2\text{M}(\text{NCS})_2\text{M}^{\text{I}}(\text{salpn})]$.

S. No.	Complex	Colour	M.P. (°C)	% Sulphur Cal (obs)	% Nitrogen Cal (obs)	C Cal (obs)	H Cal (obs)	%M Cal (obs)	%M Cal (obs)	%M Cal (obs)
1	[p-Br(C ₆ H ₄ HgSCN)] ₂ Co(NCS) ₂ Co(C ₁₇ H ₁₆ N ₂ O ₂)	Greenish	195	9.53 (9.40)	6.25 (6.10)	29.87 (29.70)	29.48 (29.30)	1.78 (1.65)	8.77 (8.60)	-
2	[p-Br(C ₆ H ₄ HgSCN)] ₂ Co(NCS) ₂ Ni(C ₁₇ H ₁₆ N ₂ O ₂)	Bluish green	182	9.47 (9.30)	6.21 (6.10)	29.68 (29.50)	29.30 (29.20)	1.77 (1.64)	4.38 (4.25)	4.37 (4.20)
3	[p-Br(C ₆ H ₄ HgSCN)] ₂ Cu(NCS) ₂ Co(C ₁₇ H ₁₆ N ₂ O ₂)	Bluish green	192	9.49 (9.28)	6.23 (6.09)	29.76 (29.60)	29.38 (29.22)	1.78 (1.63)	4.37 (4.20)	4.74 (4.60)
4	[p-Br(C ₆ H ₄ HgSCN)] ₂ Co(NCS) ₂ Zn(C ₁₇ H ₁₆ N ₂ O ₂)	Light Brown	199	9.48 (9.30)	6.22 (6.12)	29.72 (29.60)	29.34 (29.20)	1.77 (1.69)	4.36 (4.20)	4.84 (4.70)
5	[p-Br(C ₆ H ₄ HgSCN)] ₂ Ni(NCS) ₂ Co(C ₁₇ H ₁₆ N ₂ O ₂)	Light Brown	210	9.53 (9.35)	6.25 (6.13)	29.87 (29.70)	29.48 (29.38)	1.78 (1.66)	4.37 (4.18)	4.38 (4.18)
6	[p-Br(C ₆ H ₄ HgSCN)] ₂ Ni(NCS) ₂ Ni(C ₁₇ H ₁₆ N ₂ O ₂)	Brown	220	9.53 (9.30)	6.25 (6.13)	29.88 (29.72)	29.49 (29.33)	1.78 (1.66)	8.74 (8.60)	-
7	[p-Br(C ₆ H ₄ HgSCN)] ₂ Ni(NCS) ₂ Cu(C ₁₇ H ₁₆ N ₂ O ₂)	Pale Yellow	162	9.49 (9.35)	6.23 (6.10)	29.77 (29.65)	29.38 (29.28)	1.78 (1.66)	4.35 (4.15)	4.71 (4.55)
8	[p-Br(C ₆ H ₄ HgSCN)] ₂ Ni(NCS) ₂ Zn(C ₁₇ H ₁₆ N ₂ O ₂)	yellow	215	9.48 (9.48)	6.22 (6.10)	29.73 (29.68)	29.34 (29.20)	1.77 (1.70)	4.35 (4.20)	4.84 (4.70)
9	[p-Br(C ₆ H ₄ HgSCN)] ₂ Cu(NCS) ₂ Co(C ₁₇ H ₁₆ N ₂ O ₂)	Light Brown	180	9.49 (9.30)	6.23 (6.12)	29.76 (29.65)	29.38 (29.19)	1.78 (1.71)	4.35 (4.20)	4.71 (4.60)
10	[p-Br(C ₆ H ₄ HgSCN)] ₂ Cu(NCS) ₂ Ni(C ₁₇ H ₁₆ N ₂ O ₂)	Pale Yellow	186	9.49 (9.40)	6.23 (6.12)	29.77 (29.61)	29.38 (29.20)	1.78 (1.71)	4.71 (4.60)	4.35 (4.20)

Table 1: Analytical Data of The Complexes

S.No.	Complex	Colour	M.P. (°C)	% Sulphur Cal (obs)	% Mercury Cal(obs)	% Nitrogen Cal(obs)	%M Cal (obs)	%M Cal (obs)
11	[p-Br(C ₆ H ₄ HgSCN)] ₂ Cu(NCS) ₂ Co(C ₁₇ H ₁₆ N ₂ O ₂)	Green	192	9.46 (9.30)	29.66 (29.50)	6.21 (6.10)	9.39 (9.19)	-
12	[p-Br(C ₆ H ₄ HgSCN)] ₂ Zn(NCS) ₂ Co(C ₁₇ H ₁₆ N ₂ O ₂)	Dirty Brown	187	9.48 (9.33)	29.72 (29.60)	6.22 (6.12)	4.84 (4.70)	4.63 (4.20)
13	[p-Br(C ₆ H ₄ HgSCN)] ₂ Zn(NCS) ₂ Ni(C ₁₇ H ₁₆ N ₂ O ₂)	Dirty Brown	174	9.48 (9.30)	29.73 (29.62)	6.22 (6.10)	4.84 (4.70)	4.35 (4.19)
14	[p-Br(C ₆ H ₄ HgSCN)] ₂ Zn(NCS) ₂ Cu(C ₁₇ H ₁₆ N ₂ O ₂)	Pale Yellow	164	9.45 (9.28)	29.62 (29.50)	5.47 (5.30)	4.26 (4.10)	4.14 (4.03)
15	[p-Br(C ₆ H ₄ HgSCN)] ₂ Mn(NCS) ₂ Co(C ₁₇ H ₁₆ N ₂ O ₂)	Dirty White	170	9.56 (9.38)	29.96 (29.84)	6.27 (6.10)	4.10 (4.00)	4.38 (4.15)
16	[p-Br(C ₆ H ₄ HgSCN)] ₂ Mn(NCS) ₂ Ni(C ₁₇ H ₁₆ N ₂ O ₂)	Dirty White	182	9.56 (9.36)	29.96 (29.85)	6.27 (6.12)	4.10 (4.00)	4.38 (4.22)
17	[p-Br(C ₆ H ₄ HgSCN)] ₂ Mn(NCS) ₂ Cu(C ₁₇ H ₁₆ N ₂ O ₂)	Yellow	200	9.52 (9.38)	29.85 (29.70)	6.25 (6.10)	4.08 (3.85)	4.72 (4.60)

Table 2: Analytical Data of The Complexes

S.No.	Complex	Molar Conductance cm ² mhos/mole	m _{eff} (B. M.)	Molecular Weight	
				Cal.	Obs.
1	[p-Br(C ₆ H ₄ HgSCN)] ₂ Co(NCS) ₂ Co(C ₁₇ H ₁₆ N ₂ O ₂)	69.72	6.60	1343.05	1300
2	[p-Br(C ₆ H ₄ HgSCN)] ₂ Co(NCS) ₂ Ni(C ₁₇ H ₁₆ N ₂ O ₂)	59.86	4.78	1342.83	1300
3	[p-Br(C ₆ H ₄ HgSCN)] ₂ Cu(NCS) ₂ Co(C ₁₇ H ₁₆ N ₂ O ₂)	55.66	3.82	1347.66	1300
4	[p-Br(C ₆ H ₄ HgSCN)] ₂ Co(NCS) ₂ Zn(C ₁₇ H ₁₆ N ₂ O ₂)	61.43	2.00	1349.49	1295
5	[p-Br(C ₆ H ₄ HgSCN)] ₂ Ni(NCS) ₂ Co(C ₁₇ H ₁₆ N ₂ O ₂)	71.70	3.25	1342.83	1300
6	[p-Br(C ₆ H ₄ HgSCN)] ₂ Ni(NCS) ₂ Ni(C ₁₇ H ₁₆ N ₂ O ₂)	65.48	3.20	1342.61	1303
7	[p-Br(C ₆ H ₄ HgSCN)] ₂ Ni(NCS) ₂ Cu(C ₁₇ H ₁₆ N ₂ O ₂)	57.83	2.26	1347.44	1290
8	[p-Br(C ₆ H ₄ HgSCN)] ₂ Ni(NCS) ₂ Zn(C ₁₇ H ₁₆ N ₂ O ₂)	50.29	3.17	1349.27	1293
9	[p-Br(C ₆ H ₄ HgSCN)] ₂ Cu(NCS) ₂ Co(C ₁₇ H ₁₆ N ₂ O ₂)	56.38	3.85	1347.66	1290
10	[p-Br(C ₆ H ₄ HgSCN)] ₂ Cu(NCS) ₂ Ni(C ₁₇ H ₁₆ N ₂ O ₂)	49.60	3.68	1347.66	1290

Table 3: Magnetic Moment: Molar Conductance and Molecular Weight of the Complexes

11	[p-Br(C ₆ H ₄ HgSCN)] ₂ Cu(NCS) ₂ Cu(C ₁₇ H ₁₆ N ₂ O ₂)	53.63	2.10	1352.27	1300
12	[p-Br(C ₆ H ₄ HgSCN)] ₂ Zn(NCS) ₂ Cu(C ₁₇ H ₁₆ N ₂ O ₂)	62.46	4.18	1349.49	1285
13	[p-Br(C ₆ H ₄ HgSCN)] ₂ Zn(NCS) ₂ Ni(C ₁₇ H ₁₆ N ₂ O ₂)	51.45	3.12	1349.27	1280
14	[p-Br(C ₆ H ₄ HgSCN)] ₂ Zn(NCS) ₂ Cu(C ₁₇ H ₁₆ N ₂ O ₂)	47.82	1.90	1354.10	1300
15	[p-Br(C ₆ H ₄ HgSCN)] ₂ Mn(NCS) ₂ Co(C ₁₇ H ₁₆ N ₂ O ₂)	50.80	7.90	1339.06	1302
16	[p-Br(C ₆ H ₄ HgSCN)] ₂ Mn(NCS) ₂ Ni(C ₁₇ H ₁₆ N ₂ O ₂)	59.00	8.00	1338.84	1300
17	[p-Br(C ₆ H ₄ HgSCN)] ₂ Mn(NCS) ₂ Cu(C ₁₇ H ₁₆ N ₂ O ₂)	65.19	7.80	1343.67	1291

Table 4: Magnetic Moment: Molar Conductance and Molecular Weight of the Complexes

S.No.	Complexes	v(C-N) cm ⁻¹	v(C-S) cm ⁻¹	vM(NCS) cm ⁻¹	v(C-O) cm ⁻¹	v(imino gp) cm ⁻¹
1	Co(C ₁₇ H ₁₆ N ₂ O ₂)	-	-	-	1540 (s) 1520 (m)	
2	Ni(C ₁₇ H ₁₆ N ₂ O ₂)	-	-	-	1535 (s) 1525 (s)	
3	Cu(C ₁₇ H ₁₆ N ₂ O ₂)	-	-	-	1535 (s) 1525 (s)	
4	Zn(C ₁₇ H ₁₆ N ₂ O ₂)	-	-	-	1540 (s) 1520 (m)	
5	[p-Br(C ₆ H ₄ HgSCN)] ₂ Co(SCN) ₂	2920(s) 2120(s)	790 (s) 760 (s)	480 (sh) 460 (s)	-	-
6	[p-Br(C ₆ H ₄ HgSCN)] ₂ Ni(SCN) ₂	2115(w) 2100(s)	780 (s) 760 (s)	470 (s) 450 (s)	-	-
7	[p-Br(C ₆ H ₄ HgSCN)] ₂ Cu(SCN) ₂	2180(s) 2100(m)	760 (s) 740 (s)	480 (w) 440 (s)	-	-
8	[p-Br(C ₆ H ₄ HgSCN)] ₂ Zn(SCN) ₂	2160 (sb) 2100 (s)	770 (m) 740 (s)	470 (s) 450 (s)	-	-
9	[p-Br(C ₆ H ₄ HgSCN)] ₂ Mn(SCN) ₂	2180 (s) 2110 (w)	750 (w) 720 (s)	460 (m) 450 (s)	-	-

Table 5: Infrared Spectral Band Assignments of the Complexes

S.No.	Complexes	$\nu(\text{C-N})$ cm^{-1}	$\nu(\text{C-S})$ cm^{-1}	$\nu\text{M}(\text{NCS})$ cm^{-1}	$\nu(\text{C-O})$ cm^{-1}	$\nu(\text{imino gp})$ cm^{-1}
1	[p-Br(C ₆ H ₄ HgSCN)] ₂ Co(C ₁₇ H ₁₆ N ₂ O ₂)	2160(s) 2130(s)	750(s) 720(s)	460(s) 440(s)	1560(s) 1535(m)	1380(m) 1340(s)
2	[p-Br(C ₆ H ₄ HgSCN)] ₂ Co(NCS) ₂ Ni(C ₁₇ H ₁₆ N ₂ O ₂)	2180(s) 2150(s)	770(s) 730(s)	460(s) 445(s)	1550(s) 1540(s)	1380(m) 1340(s)
3	[p-Br(C ₆ H ₄ HgSCN)] ₂ Co(NCS) ₂ Cu(C ₁₇ H ₁₆ N ₂ O ₂)	2170(s) 2150(s)	760(s) 740(s)	460(s) 440(s)	1555(s) 1540(m)	1380(m) 1340(s)
4	[p-Br(C ₆ H ₄ HgSCN)] ₂ Co(NCS) ₂ Zn(C ₁₇ H ₁₆ N ₂ O ₂)	2175(s) 2100(w)	750(s) 730(s)	480(s) 430(s)	1560(s) 1540(m)	1380(s) 1340(m)
5	[p-Br(C ₆ H ₄ HgSCN)] ₂ Ni(NCS) ₂ Co(C ₁₇ H ₁₆ N ₂ O ₂)	2160(s) 2100(w)	755(s) 720(s)	490(s) 470(s)	1555(s) 1535(m)	1380(s) 1340(w)
6	[p-Br(C ₆ H ₄ HgSCN)] ₂ Ni(NCS) ₂ Ni(C ₁₇ H ₁₆ N ₂ O ₂)	2180(s) 2120(s)	760(s) 735(s)	480(s) 440(sh)	1560(s) 1540(m)	1380(s) 1340(w)
7	[p-Br(C ₆ H ₄ HgSCN)] ₂ Ni(NCS) ₂ Cu(C ₁₇ H ₁₆ N ₂ O ₂)	2170(s) 2110(s)	770(s) 750(s)	480(s) 440(sh)	1550(s) 1540(s)	1380(s) 1340(m)
8	[p-Br(C ₆ H ₄ HgSCN)] ₂ Ni(NCS) ₂ Zn(C ₁₇ H ₁₆ N ₂ O ₂)	2170(s) 2125(s)	760(s) 740(w)	460(s) 435(w)	1560(s) 1540(w)	1380(s) 1340(w)
9	[p-Br(C ₆ H ₄ HgSCN)] ₂ Cu(NCS) ₂ Cu(C ₁₇ H ₁₆ N ₂ O ₂)	2170(s) 2110(s)	760(s) 750(sh)	490(s) 440(m)	1550(m) 1540(s)	1380(s) 1340(s)
10	[p-Br(C ₆ H ₄ HgSCN)] ₂ Cu(NCS) ₂ Ni(C ₁₇ H ₁₆ N ₂ O ₂)	2190(s) 2130(s)	760(s) 740(s)	465(s) 440(sh)	1550(s) 1535(w)	1380(s) 1340(m)

Table 6: Infra- Red Spectral Band Assignments of the Complexes

S.No.	Complexes	$\nu(\text{C-N})$ cm^{-1}	$\nu(\text{C-S})$ cm^{-1}	$\nu\text{M}(\text{NCS})$ cm^{-1}	$\nu(\text{C-O})$ cm^{-1}	$\nu(\text{imino gp})$ cm^{-1}
11	[p-Br(C ₆ H ₄ HgSCN)] ₂ Cu(NCS) ₂ Cu(C ₁₇ H ₁₆ N ₂ O ₂)	2160(s) 2120(s)	760(s) 730(s)	480(s) 440(s)	1560(s) 1540(s)	1380(s) 1340(m)
12	[p-Br(C ₆ H ₄ HgSCN)] ₂ Zn(NCS) ₂ Co(C ₁₇ H ₁₆ N ₂ O ₂)	2160(s) 2100(sh)	760(s) 720(s)	470(s) 445(s)	1560(s) 1540(s)	1380(s) 1340(m)
13	[p-Br(C ₆ H ₄ HgSCN)] ₂ Zn(NCS) ₂ Ni(C ₁₇ H ₁₆ N ₂ O ₂)	2175(s) 2110(s)	770(s) 720(s)	460(s) 450(s)	1555(s) 1540(w)	1380(s) 1340(s)
14	[p-Br(C ₆ H ₄ HgSCN)] ₂ Zn(NCS) ₂ Cu(C ₁₇ H ₁₆ N ₂ O ₂)	2170(s) 2090(sh)	760(s) 730(sh)	470(s) 440(w)	1550(s) 1535(w)	1380(s) 1340(m)
15	[p-Br(C ₆ H ₄ HgSCN)] ₂ Mn(NCS) ₂ Co(C ₁₇ H ₁₆ N ₂ O ₂)	2150(s) 2090(s)	750(s) 720(w)	465(s) 440(w)	1550(s) 1535(s)	1380(s) 1340(m)
16	[p-Br(C ₆ H ₄ HgSCN)] ₂ Mn(NCS) ₂ Ni(C ₁₇ H ₁₆ N ₂ O ₂)	2170(s) 2080(s)	760(s) 730(w)	460(s) 440(w)	1560(s) 1540(m)	1380(s) 1340(m)
17	[p-Br(C ₆ H ₄ HgSCN)] ₂ Mn(NCS) ₂ Cu(C ₁₇ H ₁₆ N ₂ O ₂)	2165(s) 2120(s)	765(s) 720(m)	465(s) 720(m)	1555(s) 1535(w)	1380(s) 1340(m)

Table 7: Infra- Red Spectral Band Assignments of the Complexes

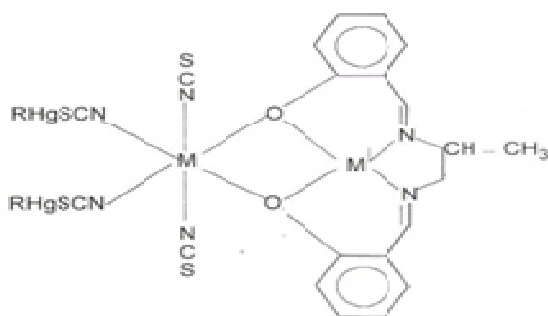
S.No.	Complexes	ν_3	ν_2	ν_1	D _q	B ¹	b
1	[p-Br(C ₆ H ₄ HgSCN)] ₂ Co(NCS) ₂ Co(C ₁₇ H ₁₆ N ₂ O ₂)	22200	15100	-	880	728	0.69
2	[p-Br(C ₆ H ₄ HgSCN)] ₂ Co(NCS) ₂ Ni(C ₁₇ H ₁₆ N ₂ O ₂)	21700	15030	-	714	859	0.87
3	[p-Br(C ₆ H ₄ HgSCN)] ₂ Co(NCS) ₂ Cu(C ₁₇ H ₁₆ N ₂ O ₂)	21000	16827	9030	889	958	0.98
4	[p-Br(C ₆ H ₄ HgSCN)] ₂ Co(NCS) ₂ Zn(C ₁₇ H ₁₆ N ₂ O ₂)	21700	17265	9220	920	945	0.96
5	[p-Br(C ₆ H ₄ HgSCN)] ₂ Ni(NCS) ₂ Co(C ₁₇ H ₁₆ N ₂ O ₂)	24200	16405	10605	943	686	0.66
6	[p-Br(C ₆ H ₄ HgSCN)] ₂ Ni(NCS) ₂ Ni(C ₁₇ H ₁₆ N ₂ O ₂)	25600	16280	10403	1038	713	0.68

Table 8: Selected Electronic Bands and Special Parameters of the Complexes

S. No	Complexes	V3	V2	V1	Dq	B ¹	β
7	[p-Br(C ₆ H ₄ HgSCN) ₂ Ni(NCS) ₂ Cu (C ₁₇ H ₁₆ N ₂ O ₂)	26300	16100	9900	1004	819	0.79
8	[p-Br(C ₆ H ₄ HgSCN) ₂ Ni(NCS) ₂ Zn (C ₁₇ H ₁₆ N ₂ O ₂)	26320	16370	9720	973	762	0.73
9	[p-Br(C ₆ H ₄ HgSCN) ₂ Co(NCS) ₂ Co (C ₁₇ H ₁₆ N ₂ O ₂)	24390	15100	9910	879	728	0.69
10	[p-Br(C ₆ H ₄ HgSCN) ₂ Co(NCS) ₂ Ni (C ₁₇ H ₁₆ N ₂ O ₂)	22165	15070	10402	693	858	0.87
11	[p-Br(C ₆ H ₄ HgSCN) ₂ Ni(NCS) ₂ Co (C ₁₇ H ₁₆ N ₂ O ₂)	21700	16315	10605	938	678	0.66
12	[p-Br(C ₆ H ₄ HgSCN) ₂ Ni(NCS) ₂ Ni (C ₁₇ H ₁₆ N ₂ O ₂)	25602	16200	10390	1038	708	0.68

Table 9: Selected Electronic Bands and Special Parameters of the Complexes

[M = Co(II), Ni(II), Cu(II), Zn(II), Mn(II), M] = Co(II), Ni(II), Cu(II), Zn(II); R=p-Bromo phenyl; salpn-(C₁₇H₁₆N₂O₂)].



[M=Co(II), Ni(II), Cu(II), Zn(II), Mn(II)]

Fig. 2

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