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STUDIES ON $(SCN)_2M(NCS)_2Hg_2(p\text{-TOLYL})_2$ AND $(SCN)_2M(NCS)_2Hg_2(\alpha\text{-NAPHTHYL})_2$ AND THEIR COMPLEXES

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Abstract—*p*-Tolyl mercury thiocyanate and α-naphthyl mercury thiocyanate react with $Co(NCS)_22py$ and form a bimetallic pink compound of formula $(py)_2(SCN)_2Co(NCS)_2Hg_2R_2$ ($R = p$-tolyl and α-naphthyl group). On heating this compound in vacuum a blue compound $(SCN)_2Co(NCS)_2Hg_2R_2$ is formed. Nickel analogues $(SCN)_2Ni(NCS)_2Hg_2R_2$ are formed by direct reaction of *p*-tolyl or α-naphthyl mercury thiocyanate with nickel thiocyanate. $(SCN)_2Co(NCS)_2Hg_2R_2$ and $(SCN)_2Ni(NCS)_2Hg_2R_2$ act as Lewis acids and form complexes with bases. The Lewis acids and their complexes with various bases have been characterized by elemental analyses, molar conductance, molecular weight, magnetic moment, infrared and electronic spectral studies. These studies reveal that both the Lewis acids are monomers. In $(SCN)_2Co(NCS)_2Hg_2R_2$ the Co(II) has tetrahedral geometry, where as in $(SCN)_2Ni(NCS)_2Hg_2R_2$ the Ni(II) has octahedral geometry through elongated axial bondings with SCN-groups of other molecules. Thiocyanate bridging of the type R–Hg–SCN–M [M = Co(II), Ni(II)] is present in the compounds. Pyridine and dimethylsulphoxide form adducts with these compounds by coordinating at Co(II) or Ni(II). The thiocyanate bridge is retained in these complexes. 2-2'bipyridyl ruptures the thiocyanate bridging in both the Lewis acids and forms cationic–anionic complexes of the type $[M(L\text{–}L)_3][RHg(SCN)_2]_2$. In both the type of complexes Co(II) and Ni(II) possess octahedral environment. The "softness" values have been used in a novel manner in proposing the structure of the complexes.

INTRODUCTION

A new class of organobimetallic compounds and their Lewis acid behaviour has been recently published by us.[1] In this communication we report the synthesis and studies of few more such compounds in which phenyl has been changed by α-naphthyl and *p*-tolyl group.

EXPERIMENTAL

Reagent grade solvents were purified before use. Cobalt and nickel thiocyanates were prepared by reacting their respective nitrates with potassium thiocyanate in ethanol. $Co(NCS)_2(py)_2$ was prepared by the method described elsewhere.[2] Dimethylsulphoxide (dmso), 2-2'bipyridyl (bipy) and pyridine (py) were used as received. *p*-Tolyl mercury chloride and α-naphthyl mercury chloride were prepared by diazotization method[3-5] as described below:

143 g (1 mmole) of α-naphthylamine was added to a mixture of 450 ml of hydrochloric acid and 500 ml of water. To the mixture 500 g of ice was added and vigorously stirred. When the temperature reached 5°C solid sodium nitrite (about 69 g) was added. After stirring for about half-an-hour, the whole mass was filtered and any residue was rejected. To the clear filtrate a cold solution of 271 g (1 mmole) of mercuric chloride in 300 ml of hydrochloric acid was slowly added with vigorous stirring. Yellow precipitate of $RN_2Cl{\cdot}HgCl_2$ was formed which was filtered after stirring for an hour. The compound was washed with water followed by acetone and dried in air. Yield 417 g. The whole compound was mixed with 114 g of copper powder in 2 l. acetone and cooled to 0°C, stirred for an hour, allowed to stand overnight and filtered. The residue was boiled with xylene, and filtered. On cooling the filtrate crystals of RHgCl were obtained. Yield 30 g.

p-Tolyl mercury chloride was similarly prepared by using *p*-toluidine in place of α-naphthylamine.

α-Naphthyl and *p*-tolyl mercury chloride were converted into their respective thiocyanates by reaction with potassium thiocyanate (BDH) in 1:1 molar ratio in acetone. KCl was filtered off, and the filtrate was concentrated by evaporation. On addition of water to the concentrate *p*-tolyl mercury thiocyanate or α-naphthyl mercury thiocyanate precipitated, which was filtered, washed with solvent, recrystallized from acetone and dried in vacuum. Yield 28 g. The purity of compounds was tested by elemental analyses and IR spectral band positions.

p-Tolyl mercury thiocyanate m.p. 210°C. (Found: *N*, 3.96; *S*, 9.12; Calc.: *N*, 4.01; *S*, 9.16%). α-Naphthyl mercury thiocyanate m.p. 155°C. (Found: *N*, 3.42; *S*, 8.29. Calc.: *N*, 3.42; *S*, 8.31%).

PREPARATION OF COMPLEXES

$(py)_2(SCN)_2Co(NCS)_2Hg_2R_2$(*R = p-tolyl and α-naphthyl*)

p-Tolyl mercury thiocyanate (6.98 g, 2 mmole) and α-naphthyl mercury thiocyanate (7.7 g, 2 mmole) were separately dissolved in 100 ml of ethanol. To each solution an ethanolic solution of $Co(NCS)_2(py)_2$ (3.33 g, 1 mmole) was added and stirred for 72 hr. A pink precipitate appeared in each case, which was filtered, washed with ethanol and dried in vacuum. Both the complexes were crystallized from a mixture of acetone and ethanol.

$(py)_2(SCN)_2Co(NCS)_2Hg_2(p\text{-tolyl})_2$—m.p. 215°C.
$(py)_2(SCN)_2Co(NCS)_2Hg_2(\alpha\text{-naphthyl})_2$—m.p. 204°C

$(SCN)_2Cl(NCS)_2Hg_2R_2$ *and* $(dmso)_2(SCN)_2Co(NCS)_2Hg_2R_2$.

On heating the pyridine complexes in vacuum the pyridine is given off and blue compounds are formed, which were recrystallized from acetone. They have the general formula $(SCN)_2Co(NCS)_2Hg_2R_2$. On reaction with pyridine their parent compounds $(py)_2(SCN)_2Co(NCS)_2Hg_2R_2$ were again formed. When ethanolic solutions of RHgSCN and $Co(NCS)_2$ were directly reacted $(SCN)_2Co(NCS)_2Hg_2R_2$ was not formed but $CoHg(SCN)_4$ was formed instead.

The dmso complexes were prepared by stirring $(SCN)_2Co(NCS)_2Hg_2$ (*p*-tolyl)$_2$ and $(SCN)_2Co(NCS)_2Hg_2$ (α-naphthyl)$_2$ in 50 ml of dimethylsulphoxide separately for 24 hr. Pink complexes were formed, which were filtered and dried in vacuum.

$(dmso)_2(SCN)_2Co(NCS)_2Hg_2(p\text{-tolyl})_2$ m.p. 215°C
$(dmso)_2(SCN)_2Co(NCS)_2Hg_2(\alpha\text{-naphthyl})_2$ m.p. 204°C.

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$[Co(bipy)_3][RHg(SCN)_2]_2$

$(SCN)_2Co(NCS)_2Hg_2$ (*p*-tolyl)$_2$ (0.873 g, 1 mmole) and $(SCN)_2Co(NCS)_2Hg_2$ (α-naphthyl)$_2$ (0.945 g, 1 mmole) were separately dissolved in 50 ml of ethanol. To each solution an ethanolic solution of 2-2′-bipyridyl (0.468 g, 3 mmole) was added and stirred for about 24 hr. Pink precipitate in each case appeared, which was filtered, washed with ethanol and dried in vacuum. The complexes were recrystallized from acetonitrile.

$[Co(bipy)_3]$[*p*-tolyl $Hg(SCN)_2]_2$ m.p. 146°C.
$[Co(bipy)_3]$[α-naphthyl $Hg(SCN)_2]_2$ m.p. 135°C.

$(SCN)_2Ni(NCS)_2Hg_2R_2$. *p*-tolyl mercury thiocyanate (6.987 g, 2 mmole) and α-naphthyl mercury thiocyanate (7.7 g, 2 mmole) were separately dissolved in acetone. To each solution a methanolic solution (1.75 g, 1 mmole) of $Ni(NCS)_2$ was added and stirred for 72 hr. A bluish-green precipitate appeared in each case which was filtered washed with methanol and dried in vacuum. The complexes were recrystallized from acetone.

$(SCN)_2Ni(NCS)_2Hg_2$(*p*-tolyl)$_2$ m.p. 238°(*d*)
$(SCN)_2Ni(NCS)_2Hg_2$(α-naphthyl)$_2$ m.p. 217°(*d*).

$(py)_2(SCN)_2Ni(NCS)_2Hg_2R_2$ *and* $[Ni(bipy)_3][RHg(SCN)_2]_2$

$(SCN)_2Ni(NCS)_2Hg_2$ (*p*-tolyl)$_2$ (0.873 g, 1 mmole) and $(SCN)_2Ni(NCS)_2Hg_2$ (α-naphthyl)$_2$ (0.945 g, 1 mmole) were separately dissolved in 50 ml of ethanol. To each solution an ethanolic solution of pyridine (0.2 ml, 2 mmole) was added, and stirred for 36 hr. Green precipitate appeared in each case and was filtered, washed with solvent and dried in vacuum. Complexes were recrystallized from acetone.

$(py)_2(SCN)_2Ni(NCS)_2Hg_2$ (*p*-tolyl)$_2$ m.p. 230°(*d*)
$(py)_2(SCN)_2Ni(NCS)_2Hg_2$ (α-naphthyl)$_2$ m.p. 255°(*d*).

The bipyridyl complexes were similarly prepared by reacting ethanolic solutions of 2,2′-bipyridyl (0.468 g, 3 mmole) in place of pyridine.

$[Ni(bipy)_3]$[*p*-tolyl $Hg(SCN)_2]_2$ m.p. 162°C.
$[Ni(bipy)_3]$[naphthyl $Hg(SCN)_2]_2$ m.p. 166°C.

The dmso complexes were prepared by the method adopted for corresponding cobalt complexes.

Analyses of the complexes. The complexes were analysed for cobalt as anthranilate, nickel as dimethylglyoximate, sulphur as sulphate and mercury gravimetrically as sulphide. Nitrogen was estimated by semi-micro Kjeldahl's method. Analytical results along with melting points are presented in Table 1.

Physical measurements. The molar conductances of the complexes were measured in dimethylformamide using a Philips conductivity bridge model PR-9500. The molecular weights were determined in dmso solution by the cryoscopic method. The magnetic susceptibility measurements were made at room temperature by Gouy's method using $CoHg(SCN)_4$ as standard. The diamagnetic correction were made using Pascal's constants. Infrared spectra of the complexes were recorded as nujol mulls or as KBr pellets on a Perkin–Elmer 621 spectrophotometer in the range 4000–200 cm^{-1} and as polyethylene disc in the range 500–50 cm^{-1} on a polytech F.I.R. 30 Fourier spectrophotometer. Electronic spectra in the range 250–1800 nm were recorded on a Carl-Zeiss DMR-21 spectrophotometer.

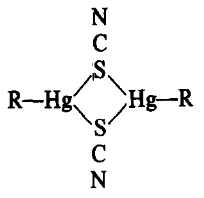
RESULTS AND DISCUSSION

$M(NCS)_2(py)_2$ or $M(NCS)_2(dmso)_2$ reacts with RHgSCN and forms an adduct of general formula $L_2(SCN)_2M(NCS)_2Hg_2R_2$ (L = py, dmso). The pyridine or dmso is given off when the adducts are heated in vacuum, leaving behind a compound of general formula $(SCN)_2M(NCS)_2Hg_2R_2$ which is termed as Lewis acid. The Lewis acids when reacted with pyridine or dmso again form the adducts. On reaction with a strong base like 2-2′bipyridyl, the Lewis acids form cationic–anionic complexes. The structure of these complexes are discussed below.

1. *Adducts.* $L_2(SCN)_2M(NCS)_2Hg_2R_2$ *and Lewis acids*—$(SCN)_2M(NCS)_2Hg_2R_2$ (L = py, dmso; M = Co, Ni and R = *p*-tolyl, α-naphthyl)

Both the adducts and the Lewis acids are non-conducting in dimethylformamide. The molecular weight data (Table 2) of $(py)_2(SCN)_2M(NCS)_2Hg_2R_2$ indicate that they are monomeric. The molecular weight of $(SCN)_2M(NCS)_2Hg_2R_2$ could not be determined on account of insufficient solubility, however, the cobalt complex may be assumed to be monomeric, on the basis of the tetrahedral coordination of the cobalt atom but the octahedral nickel complex is presumably polymeric. The adducts can be formed by reaction of pyridine or dmso with the Lewis acids which in turn can be reformed by heating the adducts in vacuum.

For deriving structural information the spectra of RHgSCN have been first studied. The solid phase spectra shows the presence of νC–N band at 2182, νC–S at 729, νHg–S at 235, δSCN at 446, and νHg–C at 459 cm^{-1}. On the basis of this information the unit cell of RHgSCN has been considered to have a dimeric centrosymmetric model, where a four membered Hg_2S_2 ring is formed.[6] The position of these bands is considerably changed when the spectrum is recorded in methanol. The νC–N is observed at 2136 and νHg–S at 283 cm^{-1}. This indicates that bridging through sulphur of thiocyanate is destroyed in solution. It has been considered safer to derive shifts from the spectral data in solution phase. On comparison of the various bands of RHgSCN with the corresponding bands of $L_2(SCN)_2M(NCS)_2Hg_2R_2$, changes are observed in νC–N, νC–S and νHg–S bands (Table 3). The νC–N band is observed in the region 2125–2170 cm^{-1} and νC–S in the region 720–795 cm^{-1}. These changes indicate that the thiocyanate of RHgSCN becomes bridging probably by coordination to M through its N-end.



A band in νC–N region in the range 2060–2080 cm^{-1} is also observed, which is assigned to N-bonded terminal thiocyanate arising from M–NCS and can be supported from its analogy to the reported band in $M(NCS)_2 2L$.[7] In the case of Lewis acids the bands assigned to νC–N, νC–S and δNCS are present almost in the same region in which they are present in their corresponding adducts.

Table 1. Analytical data of the complexes

Complexes	Colour	M.P. °C	% Sulphur		% Mercury		% Cobalt/Nickel		% Nitrogen	
			cal.	obs.	cal.	obs.	cal.	obs.	cal.	obs.
$(SCN)_2Co(NCS)_2Hg_2(p\text{-tolyl})_2$	Blue	215	14.72	14.6	44.98	45.8	6.36	6.7	6.16	6.4
$(py)_2(SCN)_2Co(NCS)_2Hg_2(p\text{-tolyl})_2$	Pink	215	12.8	12.4	37.9	38.7	5.37	5.7	5.28	5.4
$(dmso)_2(SCN)_2Co(NCS)_2Hg_2(p\text{-tolyl})_2$	Violet pink	215	12.89	12.5	37.91	38.8	5.54	5.8	5.36	5.5
$[Co(bipy)_3][p\text{-tolyl Hg}(SCN)_2]_2$	Orange pink	146	9.87	9.5	28.9	29.02	4.12	4.3	3.87	4.1
$(SCN)_2Co(NCS)_2Hg_2(\alpha\text{-naphthyl})_2$	Blue	204	13.6	13.5	41.96	42.3	5.98	6.2	5.85	5.9
$(py)_2(SCN)_2Co(NCS)_2Hg_2(\alpha\text{-naphthyl})_2$	Pink	204	11.8	11.6	36.08	36.2	5.21	5.3	5.12	5.0
$(dmso)_2(SCN)_2Co(NCS)_2Hg_2(\alpha\text{-naphthyl})_2$	Violet pink	204	11.73	11.6	36.1	36.2	5.15	5.3	5.2	5. 0
$[Co(bipy)_3][\alpha\text{-naphthyl Hg}(SCN)_2]_2$	Pink	135	9.25	9.0	28.15	28.3	4.01	4.1	4.1	3.9
$(SCN)_2Ni(NCS)_2Hg_2(p\text{-tolyl})_2$	Bluish green	238(d)	14.72	14.58	44.98	44.6	6.36	6.27	6.16	6.21
$(py)_2(SCN)_2Ni(NCS)_2Hg_2(p\text{-tolyl})_2$	Grey	230(d)	12.8	12.6	37.9	37.81	5.37	5.21	5.28	5.31
$(dmso)_2(SCN)_2Ni(NCS)_2Hg_2(p\text{-tolyl})_2$	Green	214(d)	12.89	12.62	37.91	36.98	5.54	5.14	5.36	5.12
$[Ni(bipy)_3][p\text{-tolyl Hg}(SCN)_2]_2$	Pink	162	9.87	9.5	28.9	28.54	4.12	4.25	3.87	3.75
$(SCN)_2Ni(NCS)_2Hg_2(\alpha\text{-naphthyl})_2$	Yellowish green	217(d)	13.6	13.38	41.96	41.76	5.98	5.73	5.85	5.75
$(py)_2(SCN)_2Ni(NCS)_2Hg_2(\alpha\text{-naphthyl})_2$	Grey	255(d)	11.8	11.54	36.08	36.0	5.21	5.3	5.12	4.96
$(dmso)_2(SCN)_2Ni(NCS)_2Hg_2(\alpha\text{-naphthyl})_2$	Green	226(d)	11.73	11.6	36.1	35.92	5.15	4.98	5.2	4.91
$[Ni(bipy)_3][\alpha\text{-naphthyl Hg}(SCN)_2]_2$	Pink	166	9.25	9.12	28.15	27.94	4.01	4.03	4.1	4.01

M.P. = melting point; d= decompose.

Table 2. Molar conductance and molecular weight data of the complexes

Complexes	cm^{-1} mhos/mole M/512	Molecular weight	
		cal.	obs.
$(SCN)_2Co(NCS)_2Hg_2(p\text{-tolyl})_2$	42.63	-	-
$(py)_2(SCN)_2Co(NCS)_2Hg_2(p\text{-tolyl})_2$	58.015	1031	976
$(dmso)_2(SCN)_2Co(NCS)_2Hg_2(p\text{-tolyl})_2$	65.53	1029	936
$[Co(bipy)_3][p\text{-tolyl}\ Hg(SCN)_2]_2$	136.39	-	-
$(SCN)_2Co(NCS)_2Hg_2(\alpha\text{-naphthyl})_2$	48.47	-	-
$(py)_2(SCN)_2Co(NCS)_2Hg_2(\alpha\text{-naphthyl})_2$	62.08	1103	907
$(dmso)_2(SCN)_2Co(NCS)_2Hg_2(\alpha\text{-naphthyl})_2$	66.77	1101	1035
$[Co(bipy)_3][(\alpha\text{-naphthyl}\ Hg(SCN)_2]_2$	136.11	-	-
$(SCN)_2Ni(NCS)_2Hg_2(p\text{-tolyl})_2$	57.07	-	-
$(py)_2(SCN)_2Ni(NCS)_2Hg_2(p\text{-tolyl})_2$	53.62	1031	892
$(dmso)_2(SCN)_2Ni(NCS)_2Hg_2(p\text{-tolyl})_2$	52.04	1029	947
$(SCN)_2Ni(NCS)_2Hg_2(\alpha\text{-naphthyl})_2$	70.7	-	-
$(py)_2(SCN)_2Ni(NCS)_2Hg_2(\alpha\text{-naphthyl})_2$	69.39	1103	1012
$(dmso)_2(SCN)_2Ni(NCS)_2Hg_2(\alpha\text{-naphthyl})_2$	68.05	1101	986
$[Ni(bipy)_3][\alpha\text{-naphthyl}\ Hg(SCN)_2]_2$	132.03	-	-
$[Ni(bipy)_3][p\text{-tolyl}\ Hg(SCN)_2]_2$	136.39	-	-

Table 3. Assignment of IR spectral bands

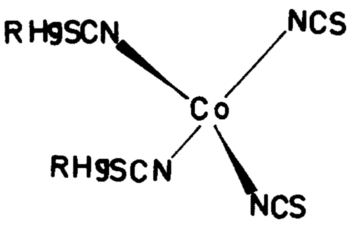
Complexes	ν C–N (cm^{-1})	ν C–S (cm^{-1})	δ NCS (cm^{-1})
$(SCN)_2Co(NCS)_2Hg_2(p\text{-tolyl})_2$	2140(s), 2060(s) 2125(sh)	760(s), 700(s)	435(s)
$(py)_2(SCN)_2Co(NCS)_2Hg_2(p\text{-tolyl})_2$	2170(s), 2080(sh)	780(s), 690(w)	430(s)
$(dmso)_2(SCN)_2Co(NCS)_2Hg_2(p\text{-tolyl})_2$	2130(vs), 2060(sh)	755(m), 715(w)	440(s)
$[Co(bipy)_3][p\text{-tolyl}\ Hg(SCN)_2]_2$	2110(sh), 2090(s)	720(vs), 705(sh)	438(s)
$(SCN)_2Co(NCS)_2Hg_2(\alpha\text{-naphthyl})_2$	2145(s), 2070(sh)	785(m), 690(s)	445(s)
$(py)_2(SCN)_2Co(NCS)_2Hg_2(\alpha\text{-naphthyl})_2$	2160(sh), 2065(s)	790(w), 700(m)	425(s)
$(dmso)_2(SCN)_2Co(NCS)_2Hg_2(\alpha\text{-naphthyl})_2$	2130(s), 2080(s)	770(vs), 745(w)	440(s)
$[Co(bipy)_3][\alpha\text{-naphthyl}Hg(SCN)_2]_2$	2090(s), 2110(sh)	715(vs), 700(sh)	430(w)
$(SCN)_2Ni(NCS)_2Hg_2(p\text{-tolyl})_2$	2170(s), 2080(m)	785(w), 745(s)	442(s)
$(py)_2(SCN)_2Ni(NCS)_2Hg_2(p\text{-tolyl})_2$	2145(s), 2070(s)	790(vs), 690(s)	425(s)
$(dmso)_2(SCN)_2Ni(NCS)_2Hg_2(p\text{-tolyl})_2$	2150(s), 2075(sh)	790(w), 725(w)	450(b)
$[Ni(bipy)_3][p\text{-tolyl}\ Hg(SCN)_2]_2$	2100(sh), 2095(s)	720(vs), 695(sh)	430(w)
$(SCN)_2Ni(NCS)_2Hg_2(\alpha\text{-naphthyl})_2$	2140(sh), 2080(s)	790(w), 740(vs)	440(s)
$(py)_2(SCN)_2Ni(NCS)_2Hg_2(\alpha\text{-naphthyl})_2$	2165(s), 2065(m)	795(w), 710(s)	434(s)
$(dmso)_2(SCN)_2Ni(NCS)_2Hg_2(\alpha\text{-naphthyl})_2$	2150(s), 2070(sh)	790(sh), 725(s)	445(w)
$[Ni(bipy)_3][\alpha\text{-naphthyl}\ Hg(SCN)_2]_2$	2105(s), 2095(sh)	705(w), 695(s)	430(s)

s= strong; sh= shoulder; m= medium; w= weak; b= broad and v= very.

The slight changes in band positions are due to change in stereochemistry around M. The change in νC–N stretching band positions due to change in stereochemistry is well described elsewhere.[8] The νM–NCS bands in the case of cobalt Lewis acids are observed at about 308 cm^{-1}, which on adduct formation shift to 240 cm^{-1}. This negative shift shows the change from tetrahedral configuration to octahedral on adduct formation.[7,9] Such a change is not observed in nickel analogues because of the presence of octahedral configuration in both the Lewis acids and their adducts. A band assigned to νM–N (py) is observed at about 270 cm^{-1} in pyridine adducts and at 378 cm^{-1} in dmso adducts which is assigned[10,11] to νM–O. These bands are absent in the Lewis acids.

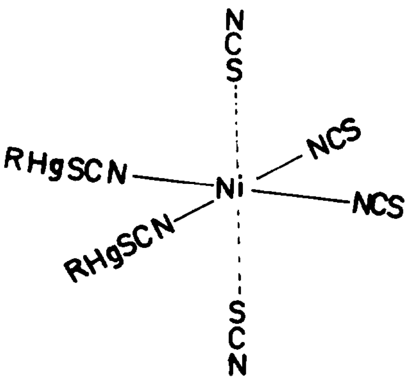
The electronic spectra of the Lewis acids and the adducts as discussed later indicate that cobalt in $(SCN)_2M(NCS)_2Hg_2R_2$ is in tetrahedral coordination and the nickel is octahedral. The octahedral geometry in case of nickel is perhaps acquired by axial coordination through sulphur of the thiocyanate group of the adjacent layer.[12] In the case of $L_2(SCN)_2M(NCS)_2Hg_2R_2$ both nickel and cobalt acquire the octahedral configuration. The magnetic moment values of $(SCN)_2Co(NCS)_2Hg_2R_2$ are 4.1–4.2 B.M. and of $L_2(SCN)_2Co(NCS)_2Hg_2R_2$ are 4.92–5.1 B.M. In the case of $(SCN)_2Ni(NCS)_2Hg_2R_2$ and their adducts these values are in the range 2.85–3.31 B.M. On the basis of above results the following structures (Figs. 1–3) can be proposed, pending confirmation by single crystal X-ray analysis. These structures are further supported by:

(I) The far IR spectra of the Lewis acids and their adducts show the presence of bands in the region 450–470, 210–220, 160–190 and 79–91 cm^{-1}, which can be assigned to νHg–C, νHg–SCN, δN–M–N and δS–Hg–C vibrations respectively.[12,13] The presence of these bands support the proposed structure.



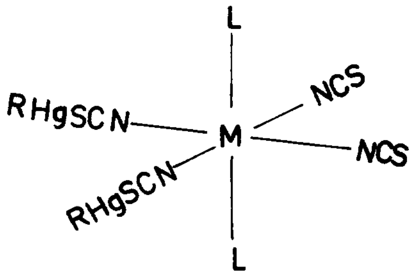
(R = p-tolyl and α-naphthyl.)

Fig. 1.



(R = p-tolyl and α-naphthyl.)

Fig. 2.



(M = Co, Ni; L = py, dmso and R = p-tolyl and α-naphthyl.)

Fig. 3.

(II) All the linkages shown in the structures are consistent with the requirements of HSAB principle.

(III) Quantitative softness values as discussed later also support various linkages.

(IV) Local symmetries around cobalt and nickel show that cobalt in $(SCN)_2M(NCS)_2Hg_2R_2$ has T_d symmetry and in $L_2(SCN)_2M(NCS)_2HgR_2$ has D_{4h} symmetry. The nickel in its Lewis acids and adducts have D_{4h} symmetry. The number of IR active bands calculated for these symmetries and the observed number of bands are in good agreement (Table 4).

(V) The cobalt and nickel are in their preferred coordination geometries in Lewis acids and in their adducts. Mercury, too has the preferred linear structure.

(VI) Organomercury halides have been shown to have poor acceptor properties,[14] hence the linkage of pyridine and dimethylsulfoxide to cobalt or nickel instead of mercury is more justified.

2. *Cationic–anionic complexes.* $[M(bipy)_3][RHg(SCN)_2]_2$

The bipyridyl complexes of both the Lewis acids show a different behaviour. Their molar conductance values (132–136 cm^{-1} mhos/moles) in dimethylformamide show that they are 1:2 electrolyte. The IR spectra of the complexes indicate the absence of bridging and N-bonded thiocyanate. Two bands in the νC–N and νC–S regions are observed which are in the range of S-bonded thiocyanate[15] (Table 3).

The electronic spectra of the complexes as discussed later indicate that cobalt and nickel are in octahedral configurations. The magnetic moment values also support this configuration. The Dq values of the complexes are close to the reported Dq values of $[Co(bipy)_3]^{2+}$ ion. The far IR spectra shows the presence of bands at 260 and 285 cm^{-1} for νCo–N and νNi–N respectively. On the basis of these observations we can suggest that the cation has cobalt or nickel duly coordinated with three molecules of bipyridyl. The anion possibly has a tricoordinated mercury linked with two S-bonded thiocyanate ions and one aryl group. The tri-coordinated structure of mercury is also supported by the number of bands in the νC–N and νC–S regions. The anion has C_{2v} symmetry and is expected to give two bands in these regions. Two bands against each are actually present. Tricoordinated mercury compounds have been reported by earlier workers also.[16,17] The preference of bipyridyl for cobalt or nickel in comparison to mercury is in conformity with the HSAB principle[18] and ΔE^{2+}_{nm}[19] requirements. The far IR spectra show the presence of

Table 4. IR spectral band assignments in the far IR region

Complexes	νHg–C (cm^{-1}) A_1+B_2	νHg–SCN (cm^{-1}) A_1+B_2	νM–NCS (cm^{-1}) $2A_1+B_1+B_2$	νM–L (cm^{-1}) A_1+B_2	δL–M–L (cm^{-1}) $2A_1+B_1+B_2$	δN–M–N (cm^{-1}) $2A_1+B_1+B_2$	δS–Hg–C (cm^{-1}) $2A_1+B_1+B_2$
$(SCN)_2Co(NCS)_2Hg_2(p\text{-tolyl})_2$	450(s)	220(s)	308(s)	-	-	178(s)	91(s)
$(py)_2(SCN)_2Co(NCS)_2Hg_2(p\text{-tolyl})_2$	452(vs)	216(b)	240(m)	285(s)	140(m)	186(m)	86(s)
$(dmso)_2(SCN)_2Co(NCS)_2Hg_2(p\text{-tolyl})_2$	452(b)	210(b)	242(m)	378(m)	162(w)	178(m)	82(s)
$[Co(bipy)_3][p\text{-tolyl Hg}(SCN)_2]_2$	468(w)	210(m)	-	260(b)	135(w)	-	84(s)
$(SCN)_2Co(NCS)_2Hg_2(\alpha\text{-naphthyl})_2$	452(vs)	220(b)	306(b)	-	-	186(s)	79(b)
$(py)_2(SCN)_2Co(NCS)_2Hg_2(\alpha\text{-naphthyl})_2$	450(s)	218(m)	239(s)	280(b)	160(m)	180(vs)	80(s)
$(SCN)_2Ni(NCS)_2Hg_2(p\text{-tolyl})_2$	468(s)	216(s)	242(s)	-	-	190(m)	80(s)
$(SCN)_2Ni(NCS)_2Hg_2(\alpha\text{-naphtyl})_2$	470(vs)	220(w)	238(b)	-	-	160(m)	79(s)
$(py)_2(SCN)_2Ni(NCS)_2Hg_2(\alpha\text{-naphtyl})_2$	468(vs)	215(b)	242(m)	270(s)	132(w)	182(w)	82(w)
$[Ni(bipy)_3][p\text{-tolyl Hg}(SCN)_2]_2$	458(vs)	210(m)	-	285(vs)	125(b)	-	86(s)

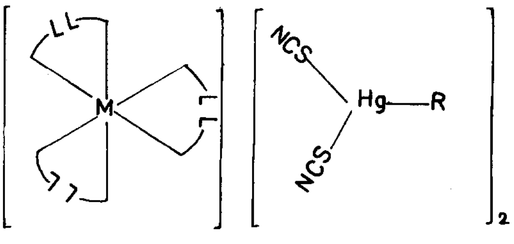
s= strong; m= medium; b= broad; w= weak; and v= very.

Hg-SCN band at 210 cm^{-1} and absence of νCo–NCS or νNi–NCS band.

On the basis of these results the following structure (Fig. 4) can be proposed to cationic–anionic complexes.

Electronic spectra. The electronic spectra of the complexes have been recorded as nujol mulls in order to avoid the effect of solvolysis in solution. In the case of $(SCN)_2Co(NCS)_2Hg_2$ two intense bands assigned to ${}^4A_2 \rightarrow {}^4T_2(F)$ (ν_3), and ${}^4A_2 \rightarrow {}^4T_1(P)$ (ν_2) transitions were observed at about 16,400 and 7850 cm^{-1} respectively. The ν_2 band was not split showing the presence of T_d symmetry around cobalt. The Dq values derived from ν_3 and ν_2 bands are about 480 cm^{-1}. This value is higher than the reported[20] Dq value of $[Co(NCS)_4]^{2+}$. This increase in ligand field strength is consistent with the Cotton's observation.[20] It has been reported that when the free sulphur end of N-coordinated thiocyanate ions become bound to other ions such as Hg^{2+} the contribution of the N-coordinated thiocyanate to the ligand field around the first metal is enhanced. In $L_2(SCN)_2Co(NCS)_2Hg_2R_2$, three bands in the region 20,830–21,600, 16,500–17,800 and 8000–8900 cm^{-1} are observed assignable to ${}^4T_{1g} \rightarrow {}^4T_{1g}(P)$ (ν_3), ${}^4T_{1g} \rightarrow {}^4A_{2g}(\nu_2)$ and ${}^4T_{1g} \rightarrow {}^4T_{2g}(\nu_1)$ transitions respectively. The ν_2 band being two-electron transition is very weak. The spectral parameters Dq, B′ and β have been calculated from ν_2 and ν_3 bands. The Dq values so obtained have been compared with ν_1 band position and both are very close. The band position, spectral parameters and the magnetic moment values (Table 5) support octahedral configuration around cobalt in the adducts. In case of cationic–anionic complexes three bands are also observed which are assigned to ${}^4T_{1g} \rightarrow {}^4T_{1g}(P)(\nu_3)$, ${}^4T_{1g} \rightarrow {}^4A_{2g}(\nu_2)$ and ${}^4T_{1g} \rightarrow {}^4T_{2g}(\nu_1)$ transitions. These bands are present in the region 21,260–21,600, 16,490–17,710 and 8920–9300 cm^{-1} respectively. The position of the bands in case of the cationic–anionic complexes have higher value as compared to corresponding band positions of the pyridine adducts. The Dq value (945 cm^{-1}) of the cation$[Co(bipy)_3]^{2+}$ is higher than the Dq values (890 cm^{-1}) of the adducts. $[Co(bipy)_3]^{2+}$ is expected to have higher value than $L_2(SCN)Co(NCS)_2Hg_2R_2$. The higher Dq value supports the existence of such a cation.

The electronic spectra of the nickel Lewis acids, their adducts and cationic–anionic complexes show the presence of three bands in the region 25,640–28,570, 15,870–18,500 and 9010–11,360 cm^{-1} which are assigned to ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)(\nu_3)$, ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)(\nu_2)$ and ${}^3A_{2g} \rightarrow {}^3T_{2g}(F)(\nu_1)$ respectively. The Dq values derived from ν_2 and ν_3 bands or from ν_1 bands show that Lewis acid has the lowest value and the cationic–anionic complexes have the highest value. This difference in Dq values is perhaps due to the difference in moieties around nickel in all the three cases. In the Lewis acid the nickel has $(NCS)_2Ni(NCS)_2$ moiety and in the adducts has $L_2Ni(NCS)_4$ and in the cationic–anionic complexes has $[Ni(bipy)_3]$ moiety. The thiocyanate being at the weaker and of the spectrochemical series will have a lower Dq value than bipyridyl which is at the stronger end of the spectrochemical series. The highest Dq value in case of cationic–anionic complexes and its closeness to the reported[21] Dq value of $[Ni(bipy)_3]^{2+}$, indicates that nickel is linked only with bipyridyl.



(M = Co, Ni; L = bipyridyl- and R = p-tolyl and α-naphthyl).

Quantitative "softness" values

Quantitative "softness" values of metal ions in different compounds and of ligands, have recently been used in deriving choice of linkages in a complex, its structures and relative metal ligand bond strength.[18,19,22,23] The "softness" of metal ions has been denoted by $E_n{}^{2+}$ and of bases by $E_m{}^{2+}$, and the difference between the two by ΔE^{2+}_{nm}. The "softness" values of various metal ions and bases involved in the present series have also been calculated by the method described elsewhere,[19] and are presented in Table 6. These values have been applied in the following manner:

(1) The pyridine, dmso or bipyridyl when reacted with any of the Lewis-acids has two sites for linkage, one at M[Co(II) or Ni(II) or Zn(II)] and the other at mercury. The ΔE^{2+}_{nm} values derived for M–py linkage and Hg–py linkage show that the former will be preferred because of higher value of ΔE^{2+}_{nm} (Table 7). The experimental results also support this linkage.

(2) The difference in total "softness" $\Delta TE_n{}^{2+}$(M–Hg) values of M and Hg has been indicative of the stability of thiocyanate bridge between M and Hg.[23] The difference in total "softness" between M(II) and Hg(II) of the three Lewis acids of the alkyl series (Table 8) shows the following order of the stability of the thiocyanate bridge: Ni–Hg > Co–Hg > Zn–Hg.

The difference in total "softness" values in Zn–Hg Lewis acids is the lowest, hence the thiocyanate bridge between these two metal ions is the weakest. On reaction with pyridine Co–Hg Lewis acids form adducts, whereas in case of Zn–Hg Lewis acid the thiocyanate bridge in between Zn–Hg is broken. This may be on account of lower $\Delta TE_n{}^{2+}$(Zn–Hg) value. It is interesting to note that Zn–Hg Lewis acid of *p*-tolyl forms adducts with pyridine. The $\Delta TE_n{}^{2+}$(Zn–Hg) derived for this Lewis acid is 14.449 which is, higher as compared to alkyl series, and it is perhaps on this account the thiocyanate bridge between Zn–Hg is stable.

(3) Metal ligand bond strength has recently been represented in terms of matching constant.[19] The matching constant data in case of Lewis acids and their adducts have been calculated by the following equation and are presented in Table 9.

$$\text{Matching constant} = |E_n{}^{2+} - E_m{}^{2+}| + \text{CFSE}.$$

A reference to Table 9 shows that the complexes where M = Ni(II) have higher value than the corresponding cobalt complexes. The zinc analogues have the lowest value. The sequence of stability is in consonance with the Irving-Williams stability sequence.[24] The matching constant value also indicate that the -naphthyl complexes are comparatively more stable than the *p*-tolyl complexes.

Table 5. Selected electronic bands and their spectral parameters

Complexes	ν_3 (cm^{-1})	ν_2 (cm^{-1})	ν_1 (cm^{-1})	Dq (cm^{-1})	B' (cm^{-1})	β	μ_{eff} (B.M.)
$(SCN)_2Co(NCS)_2Hg_2$(p-tolyl)$_2$	16,400	7,850	-	480	642	.66	4.1
$(py)_2(SCN)_2Co(NCS)_2Hg_2$(p-tolyl)$_2$	20,830	16,680	8,900	890	941	.97	4.92
$(dmso)_2(SCN)_2Co(NCS)_2Hg_2$(p-tolyl)$_2$	21,600	17,800	8,010	794	806	.83	4.94
$[Co(bipy)_3]$[p-tolyl Hg$(SCN)_2]_2$	21,260	16,490	8,920	890	941	.97	4.99
$(SCN)_2Co(NCS)_2Hg_2$(α-naphthyl)$_2$	16,390	7,840	-	475	757	.78	4.2
$(py)_2(SCN)_2Co(NCS)_2Hg_2$(α-naphthyl)$_2$	21,270	17,000	8,800	908	961	.99	5.1
$(dmso)_2(SCN)_2Co(NCS)_2Hg_2$(α-naphthyl)$_2$	21,270	16,500	8,000	755	728	.75	5.1
$[Co(bipy)_3]$[α-naphthyl Hg$(SCN)_2]_2$	21,600	17,710	9,300	945	961	.99	5.04
$(SCN)_2Ni(NCS)_2Hg_2$(p-tolyl)$_2$	27,790	16,650	9,620	1,020	906	.87	3.07
$(py)_2(SCN)_2Ni(NCS)_2Hg_2$(p-tolyl)$_2$	28,570	17,390	10,530	1,073	916	.88	2.99
$(dmso)_2(SCN)_2Ni(NCS)_2Hg_2$(p-tolyl)$_2$	26,315	16,130	9,010	1,005	812	.78	3.18
$[Ni(bipy)_3]$[p-tolyl Hg$(SCN)_2]_2$	27,200	17,800	11,360	1,114	770	.74	2.85
$(SCN)_2Ni(NCS)_2Hg_2$(α-naphthyl)$_2$	27,780	16,670	9,610	1,085	906	.87	3.14
$(py)_2(SCN)_2Ni(NCS)_2Hg_2$(α-naphthyl)$_2$	25,640	18,500	10,860	1,057	958	.92	3.08
$(dmso)_2(SCN)_2Ni(NCS)_2Hg_2$(α-naphthyl)$_2$	26,300	15,870	9,170	1,007	729	.70	3.31
$[Ni(bipy)_3]$[α-naphthyl Hg$(SCN)_2]_2$	26,940	16,500	10,900	1,057	698	.67	3.08

Table 6. Effective "softness" values of metals and ligands

Complexes	$E^{\ddagger}_{n(eff)}$ (Co)	$E^{\ddagger}_{n(eff)}$ (Ni)	$E^{\ddagger}_{n(eff)}$ (Zn)	$E^{\ddagger}_{n(eff)}$ (Hg)	$E^{\ddagger}_{m}$ (py) N-end	$E^{\ddagger}_{m}$ (dmso) O-end	$E^{\ddagger}_{m}$ $(SCN)^-$ N-end	$E^{\ddagger}_{m}$ $(NCS)^-$ S-end	$E^{\ddagger}_{m}$ (RHgSCN) N-end
$(SCN)_2M(NCS)_2Hg_2$(p-tolyl)$_2$	-3.34	-4.062	-5.003	-6.431	-	-	-12.65	-8.22	-11.412
$(SCN)_2M(NCS)_2Hg_2$(α-naphthyl)$_2$	-3.269	-4.032	-	-6.414	-	-	-12.65	-8.22	-11.393
$(py)_2(SCN)_2M(NCS)_2Hg_2$(p-tolyl)$_2$	-3.297	-4.067	-5.102	-6.431	-11.49	-	-12.65	-8.22	-11.412
$(py)_2(SCN)_2M(NCS)_2Hg_2$(α-naphthyl)$_2$	-3.281	-3.956	-	-6.414	-11.49	-	-12.65	-8.22	-11.393
$(dmso)_2(SCN)_2M(NCS)_2Hg_2$(p-tolyl)$_2$	-3.217	-3.979	-	-6.431	-	-10.87	-12.65	-8.22	-11.412
$(dmso)_2(SCN)_2M(NCS)_2Hg_2$(α-naphthyl)$_2$	-3.202	-3.965	-	-6.414	-	-10.87	-12.65	-8.22	-11.393

The softness values of the metals and the ligands have been calculated in the solvent ethanol.

Table 7. Matching (ΔE^{2+}_{nm}) between metals and ligands

Ligands	ΔE^+_{nm}(Co-L)	E^+_{nm}(Ni-L)	ΔE^+_{nm}(Zn-L)	ΔE^+_{nm}(Hg-L)
pyridine	10.75	10.97	7.171	6.14
dmso	10.49	10.71	6.552	5.88
2-2′ bipyridyl	11.06	11.28	7.121	6.45

The matching (ΔE^+_{nm}) has been derived from the difference in softness values of metal ions and the ligand.[19] The higher is the value of ΔE^+_{nm} the better is the matching. E^{2+} of *metal ions*:—$Co^{+2} = -0.38$, $Ni^{2+} = -0.16$, $Zn^{2+} = -4.318$ and $Hg^{2+} = -4.99$.

Table 8. Total "softness" difference "ΔTE^{2+}_n(M(Hg)" values

Lewis acids	$\Delta TE_n{}^+$(Co–Hg)	$\Delta TE_n{}^+$(Ni–Hg)	$\Delta TE_n{}^+$(Zn–Hg)
$(SCN)_2M(NCS)_2Hg_2(CH_3)_2$	14.48	16.65	13.10
$(SCN)_2M(NCS)_2Hg_2(C_2H_5)_2$	14.34	16.47	12.97
$(SCN)_2M(NCS)_2Hg_2(C_3H_7)_2$	11.94	12.77	11.46
$(SCN)_2M(NCS)_2Hg_2(C_4H_9)_2$	14.24	16.33	12.97

$\Delta TE_n{}^+$(M–Hg) have been calculated by adopting the equation reported elsewhere.[22]

Table 9. Matching constant values of the complexes

Complexes	Dq (cm^{-1})	CFSE (cm^{-1})	CFSE (e.v)	ΔE^+_{nm}	Matching constant (ΔE^+_{nm} + CFSE)
$(SCN)_2Co(NCS)_2Hg_2(p\text{-tolyl})_2$	480	39,840	4.939	9.309	14.248
$(SCN)_2Co(NCS)_2Hg_2(\alpha\text{-naphthyl})_2$	475	39,900	4.947	9.380	14.327
$(SCN)_2Ni(NCS)_2Hg_2(p\text{-tolyl})_2$	1020	53,760	6.665	8.587	15.252
$(SCN)_2Ni(NCS)_2Hg_2(\alpha\text{-naphthyl})_2$	1026	53,668	6.656	8.618	15.274
$(SCN)_2Zn(NCS)_2Hg_2(p\text{-tolyl})_2$	0-	-	-	7.546	7.546
$(py)_2(SCN)_2Co(NCS)_2Hg_2(p\text{-tolyl})_2$	890	38,480	4.770	8.193	12.963
$(py)_2(SCN)_2Co(NCS)_2Hg_2(\alpha\text{-naphthyl})_2$	908	38,336	4.753	8.208	12.961
$(py)_2(SCN)_2Ni(NCS)_2Hg_2(p\text{-tolyl})_2$	1073	53,124	6.586	7.428	14.014
$(py)_2(SCN)_2Ni(NCS)_2Hg_2(\alpha\text{-naphthyl})_2$	1057	53,688	6.656	8.618	15.274
$(py)_2(SCN)_2Zn(NCS)_2Hg_2(p\text{-tolyl})_2$	-	-	-	6.422	6.422
$(dmso)_2(SCN)_2Co(NCS)_2Hg_2(p\text{-tolyl})_2$	794	39,248	4.866	7.653	12.519
$(dmso)_2(SCN)_2Co(NCS)_2Hg_2(\alpha\text{-naphthyl})_2$	756	39,552	4.904	7.667	12.571
$(dmso)_2(SCN)_2Ni(NCS)_2Hg_2(p\text{-tolyl})_2$	1,005	53,940	6.687	6.89	13.577
$(dmso)_2(SCN)_2Ni(NCS)_2Hg_2(\alpha\text{-naphthyl})_2$	1,007	53,316	6.609	7.533	14.142

Comparison with alkyl mercury thiocyanate complexes

(1) Alkyl mercury thiocyanate RHgSCN–[R = CH_3, C_2H_5, C_3H_7, C_4H_9, C_5H_{11}] react with $Co(NCS)_2$ and form the Lewis acids of general formula $(SCN)_2Co(NCS)_2Hg_2R_2$. The aryl mercury thiocyanates ArHgSCN–[Ar = C_6H_5, $CH_3C_6H_4$, $C_{10}H_7$] do not react with $Co(NCS)_2$, to form the corresponding Lewis acids. They however, react with $Co(NCS)_2(py)_2$ and form adducts of general formula $(py)_2(SCN)_2Co(NCS)_2Hg_2(Ar)_2$. On heating these adducts in vacuum, the pyridine is given off and Lewis acids are formed.

(2) The dimethylsulphoxide forms stable complexes with aryl derivatives whereas the dmso complexes of alkyl derivatives are very unstable.

(3) The Dq values of $(SCN)_2Ni(NCS)_2Hg_2R_2$ (R = methyl, ethyl, propyl, butyl, amyl, *p*-tolyl and α-naphthyl) as presented in parentheses indicate th at *n*-amyl mercury thiocyanate has the highest ligand field strength and the *n*-propyl mercury thiocyanate has the lowest. The spectrochemical series can be drawn in the following order.

n-$C_5H_{11}HgSCN(1070) > \alpha$-$C_{10}H_7HgSCN(1026)$
$> \alpha$-$CH_3C_6H_4HgSCN(1020)$
$C_2H_5HgSCN(1018) > CH_3HgSCN(1016)$
$> n$-$C_4H_9HgSCN(1015)$
$C_3H_7HgSCN(1014)$.

(4) When Co(II) and Ni(II) are replaced by Zn(II) in the Lewis acids the behaviour become entirely different in alkyl and aryl analogs. On reaction with pyridine the alkyl derivative-$(SCN)_2Zn(NCS)_2Hg_2R_2$ decompose

whereas the aryl analogs $(SCN)_2Zn(NCS)_2Hg_2Ar_2$ forms well defined complexes.

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