Complexes of n- and iso-Propyl Mercury Selenocyanates with Cobalt and Nickel Thiocyanates

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n- and iso-propyl mercury selenocyanates have been reacted with thiocyanates of Co(II) and Ni(II). Cobalt and nickel thiocyanates form complexes of general formula $(SCN)_2M(NCSeHgR)_2$ [M = Co(II), Ni(II); R = n-propyl and iso-propyl]. These complexes have also been reacted with pyridine and 2,2'-bipyridine. Pyridine forms non-conducting adducts whereas the 2,2'-bipyridine forms cationic–anionic complexes.

Introduction

Recently Singh *et al.* [1] reported a new class of bimetallic mixed dithiocyanato-diselenocyanato compounds (SCN)(SeCN)M(NCS)(NCSe)Hg, M = Co(II), Ni(II) and their complexes with certain Lewis-bases. We report in this communication the corresponding organobimetallic mixed dithiocyanato-diselenocyanato compounds and their complexes.

Experimental

Reagent grade solvents were purified before use. $n\text{-}C_3H_7HgCl$ and $iso\text{-}C_3H_7HgCl$ were prepared using Grignard reagents. The chlorides were converted into selenocyanate by stirring an acetone solution of $n\text{-}C_3H_7HgCl$ with an acetone solution of KNCSe in a 1:1 molar ratio. The precipitated KCl was filtered off and the filtrate was added slowly into well-stirred ether. $n\text{-}C_3H_7HgSeCN$ precipitated as a white crystalline powder, which was filtered, washed with light petrol and dried in a vacuum. The iso-propyl analogue was similarly prepared. *Anal.* Calcd. for $n\text{-}C_3H_7HgSeCN$: C, 10.34; H, 2.01; Se, 22.70; Hg, 57.4; N, 4.02%. Found: C, 10.00; H, 1.99; Se, 22.35; Hg, 56.95; N, 3.99. M.p. 55 °C (decompose); yield 70%; IR (Nujol): 2150 (ν(CN)), 540 (ν(CSe)), 395 cm^{-1} (δ(NCSe)), IR (in acetone) 2148 (ν(CN)), 540 (ν(CSe)), 395 cm^{-1} (δ(NCSe)). *Anal.* Calcd. for $iso\text{-}C_3H_7HgSeCN$: C, 10.34; H, 2.01; Se, 22.70; Hg, 57.4; N, 4.02. Found: C, 10.05; H, 2.00; Se, 22.45; Hg, 57.00; N, 3.99%. M.p. 47 °C (decompose), yield 70%; IR (Nujol): 2140 (ν(CN)), 540 (ν(CSe)), 400 cm^{-1} (δ(NCSe)), IR (in acetone 2135 (ν(CN)), 540 (ν(CSe), 395 cm^{-1} (δ(NCSe)).

Preparation of Lewis-acids: $(SCN)_2M(NCSeHgR)_2$ M = Co(II), Ni(II) and R = $n\text{-}C_3H_7$, $iso\text{-}C_3H_7$

$(SCN)_2Co(NCSeHgR)_2$

1.75 g of $Co(NCS)_2$ and 6.9 g of $n\text{-}C_3H_7HgSeCN$ were dissolved in 50 ml of acetone respectively in two separate flasks. The solutions were mixed, kept in an ice-bath and stirred for an hour. A green compound was formed, filtered, washed with acetone and dried *in vacuo.* Iso-propyl analogues were similarly prepared: the n-propyl derivative has m.p. 145 °C and that from iso-propyl 155 °C.

$(SCN)_2Ni(NCSeHgR)_2$

A solution of 1.75 g of $Ni(NCS)_2$ in 25 ml of methanol was mixed with a solution of 6.9 g of $n\text{-}C_3H_7HgSeCN$ in 100 ml of acetone, and the mixture was stirred for 1 h in the dark. A sky blue compound was formed which was filtered, washed with acetone and dried under vacuum. The iso-propyl analogue was similarly prepared. The n-propyl derivative melts at 160 °C and the iso-propyl derivative at 165 °C, with decomposition.

Preparation of Adducts and Cationic–Anionic Complexes: Adducts: $(py)_2(SCN)_2M(NCSeHgR)_2$, M = Co(II), Ni(II) Cationic–Anionic Complexes: $[M(L-L)_3][RHg(SCN)(SeCN)]_2$, L–L = 2,2'-bipyridine, M = Co(II), Ni(II)

The complexes were prepared by mixing in stoichiometric ratios a suspension of the $(SCN)_2M(NCSeHgR)_2$ in ethanol with a solution of the ligand in the same solvent and stirring the mixture for 12 h. Pink compounds were formed in the case of Co(II), and light blue in the case of Ni(II) complexes. They were filtered, washed with ethanol and dried under vacuum. Complexes with pyridine were recrystallized from acetone and 2,2'-bipyridine were recrystallized from a mixture of ethanol and dimethylsulphoxide.

Analyses of the complexes and various physical measurements were made as described earlier [1].

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TABLE I. Analytical Data of the Complexes.

Complexes	Colour	M.P.[a] °C	% Se		% Co/Ni		% S		% N		% Hg	
			cal.	obs.	cal.	obs.	cal.	obs.	cal.	obs.	cal.	obs.
$(SCN)_2Co(NCSeHg\ n\text{-}C_3H_7)_2$	Green	145	18.11	17.95	6.76	6.25	7.33	7.00	6.42	6.05	45.98	45.35
$(SCN)_2Co(NCSeHg\ iso\text{-}C_3H_7)_2$	Green	155	18.11	17.92	6.76	6.15	7.33	7.10	6.42	6.20	45.98	45.25
$(SCN)_2Ni(NCSeHg\ n\text{-}C_3H_7)_2$	Sky blue	160	18.11	18.00	6.76	6.28	7.33	6.99	6.42	6.00	45.98	45.32
$(SCN)_2Ni(NCSeHg\ iso\text{-}C_3H_7)_2$	Sky blue	165	18.11	17.94	6.76	6.34	7.33	6.98	6.42	6.10	45.98	45.40
$(py)_2(SCN)_2Co(NCSeHg\ n\text{-}C_3H_7)_2$	Pink	128	15.33	15.20	5.72	5.35	6.21	6.00	5.43	5.27	38.85	38.35
$(py)_2(SCN)_2Co(NCSeHg\ iso\text{-}C_3H_7)_2$	Pink	132	15.33	15.24	5.72	5.25	6.21	5.99	5.43	5.10	38.85	38.42
$(py)_2(SCN)_2Ni(NCSeHg\ n\text{-}C_3H_7)_2$	Light blue	138	15.33	15.15	5.72	5.32	6.21	6.00	5.43	5.12	38.85	38.45
$(py)_2(SCN)_2Ni(NCSeHg\ iso\text{-}C_3H_7)_2$	Light blue	142	15.33	15.05	5.72	5.52	6.21	6.05	5.43	5.05	38.85	38.35
$[Co(bipy)_3][(SCN)(SeCN)Hg\ n\text{-}C_3H_7]_2$	Brown	168	11.79	11.65	4.40	4.20	4.77	4.60	4.17	3.98	29.92	29.45
$[Co(bipy)_3][(NCS)(NCSe)Hg\ iso\text{-}C_3H_7]_2$	Brown	170	11.79	11.48	4.40	4.30	4.77	4.52	4.17	3.95	29.92	29.55
$[Ni(bipy)_3][(NCS)(NCSe)Hg\ n\text{-}C_3H_7]_2$	Light pink	175	11.79	11.52	4.40	4.15	4.77	4.32	4.17	4.05	29.92	29.35
$[Ni(bipy)_3][(NCS)(NCSe)Hg\ iso\text{-}C_3H_7]_2$	Light pink	178	11.79	11.65	4.40	4.05	4.77	4.45	4.17	3.97	29.92	29.45

[a] Melt with decomposition.

Results and Discussion

$(SCN)_2M(NCSeHgR)_2$

RHgSeCN has eight atoms in a molecule and is non-linear, and hence has eighteen fundamental vibrations. The modes associated with the C–Hg–Se–C–N skeleton are, ν(C–N)(A′), ν(CSe)(A′), ν(Hg–Se)(A′), ν(Hg–C)(A′) and δ(NCSe)(A′) + (A″). The number of bands observed in particular regions are consistent with the expected number, except a weak extra band which appears in the ν(C–N) region at 2090 cm^{-1}. RHgSeCN has C_s symmetry [2]. The solution spectra in acetone has been examined in the νC–N region. The position of the band in the solid and solution phase remain the same but the band observed at 2090 cm^{-1} in the solid phase disappears. The band at 2150 cm^{-1} is assigned to ν(CN), at 540 cm^{-1} to ν(CSe) and at 395 cm^{-1} to δ(NCSe). On reaction with $M(NCS)_2$ a complex of general formula $(SCN)_2M(NCSHgR)_2$ is formed. On complex formation two bands at 2170 and 2090 cm^{-1} appear for ν(CN) at 820 and 540 cm^{-1} for ν(CX) X = Se or S and at 480 and 420 cm^{-1} for δ(NCX). This change indicates that the selenocyanate of RHgSeCN becomes bridging on complex formation [3].

The electronic spectrum of $(SCN)_2Co(NCSeHgR)_2$ shows the presence of two intense bands due to d–d transitions in the region 16500 cm^{-1} and 8000 cm^{-1} assigned to $^4A_2 \rightarrow {}^4A_2(F)\ (\nu_3)$ and $^4A_2 \rightarrow {}^4T_1(F)\ (\nu_2)$ transitions, respectively. Similarly the nickel counterparts show the presence of three band in the region 26600–27000, 16300–16950, 9900–10200 cm^{-1} assigned to $^3A_{2g} \rightarrow {}^3T_{1g}\ (\nu_3)$, $^3A_{2g} \rightarrow {}^3T_{1g}(\nu_2)$ and $^3A_{2g} \rightarrow {}^3T_{2g}\ (\nu_1)$, respectively. The positions of these bands and spectral parameters derived from them suggest tetrahedral geometry around Co(II) [4] and octahedral environment around Ni(II), probably by coordinating selenocyanate groups of other molecules [5]. The magnetic moment values also support the same geometry.

Adducts: $(py)_2(SCN)_2M(NCSeHgR)_2$

Pyridine reacts with $(SCN)_2M(NCSeHgR)_2$ and forms pink complexes in case of Co(II) and light blue in case of nickel(II). They are non-conducting in dimethylformamide [6] and are partly dissociated in dimethylsulphoxide solution. Electronic spectra of the Co(II) complexes in solid phase give bands in the region 20190–21440, 16340–18700 and 9000–9700 cm^{-1} assigned to $^4T_{1g} \rightarrow {}^4T_{1g}(P)\ (\nu_3)$, $^4T_1 \rightarrow {}^4A_{2g}(\nu_2)$ and $^4T_{1g} \rightarrow {}^4T_{2g}(\nu_1)$ transitions, respectively. Similarly the electronic spectra of nickel analogues also indicate the presence of three bands in the range 27550–27800 cm^{-1}, 17200–16850 cm^{-1} and 10500–10490 cm^{-1} assignable to $^3A_{2g} \rightarrow {}^3T_{2g}(P)\ (\nu_3)$, $^3A_{2g} \rightarrow {}^3T_{1g}(P)\ (\nu_2)$ and $^3A_{2g} \rightarrow {}^3T_{2g}\ (\nu_1)$ transitions, respectively. The positions of these bands, spectral parameters and magnetic moment values

TABLE II. Infrared Spectral Band Assignments of the Complexes (cm^{-1}).[a]

Complexes	ν(CN)	ν(CX)	ν(HgC)	δ(NCX)	ν(ML)
$(SCN)_2Co(NCSeHg\ n\text{-}C_3H_7)_2$	2170s, 2120s 2090m	820m, 540s	535m	480s, 420m	
$(SCN)_2Co(NCSeHg\ iso\text{-}C_3H_7)_2$	2175s, 2110s 2088m	815m, 535s	528m	475s, 425m	
$(SCN)_2Ni(NCSeHg\ n\text{-}C_3H_7)_2$	2170s, 2100m 2085m	825m, 550s	530m	480s, 405m	
$(SCN)_2Ni(NCSeHg\ iso\text{-}C_3H_7)_2$	2175 s, 2115w 2080m	818m, 545s	525m	475s, 410w	
$(py)_2(SCN)_2Co(NCSeHg\ n\text{-}C_3H_7)_2$	2180s, 2115sh 2084m	810m, 538m	530s	475s, 425s	245m
$(py)_2(SCN)_2Ni(NCSeHg\ n\text{-}C_3H_7)_2$	2178s, 2100s 2090s	816m, 535m	525m	465s, 395m	235m
$[Co(bipy)_3][(NCS)(NCSe)Hg\ n\text{-}C_3H_7]_2$	2130s, 2100s	735s, 535m	525w	465m, 390w	245s
$[Ni(bipy)_3][(NCS)(NCSe)Hg\ n\text{-}C_3H_7]_2$	2120sh, 2100s	745s, 545s	535m	475s, 390m	250m

[a] s = strong, sh = shoulder, m = medium and w = weak.

TABLE III. Electronic Spectral Band Positions and Magnetic Moment Data.

Complexes	ν_3 cm^{-1}	ν_2 cm^{-1}	ν_1 cm^{-1}	Dq cm^{-1}	B'	β	$\mu_{eff.}$ (B.M.)
$(SCN)_2Co(NCSeHg\ n\text{-}C_3H_7)_2$	16430	8000	–	429	905	0.93	4.55
$(SCN)_2Co(NCSeHg\ iso\text{-}C_3H_7)_2$	16660	8000	–	415	875	0.90	4.60
$(SCN)_2Ni(NCSeHg\ n\text{-}C_3H_7)_2$	26600	16350	10500	1016	832	0.80	2.98
$(SCN)_2Ni(NCSeHg\ iso\text{-}C_3H_7)_2$	27000	16500	10250	1026	848	0.82	2.95
$(py)_2(SCN)_2Co(NCSeHg\ n\text{-}C_3H_7)_2$	20200	17000	9000	870	925	0.95	5.10
$(py)_2(SCN)_2Ni(NCSeHg\ n\text{-}C_3H_7)_2$	27700	16800	10400	1035	825	0.90	3.10
$[Co(bipy)_3][(NCS)(NCSe)Hg\ n\text{-}C_3H_7]_2$	20920	16950	9100	905	944	0.97	4.90
$[Ni(bipy)_3][(NCS)(NCSe)Hg\ n\text{-}C_3H_7]_2$	27390	16810	10050	1040	866	0.84	3.05

indicate that Co(II) and Ni(II) are in an octahedral coordination configuration [7]. The positions of ν(CN), ν(CX) and δ(NCX) bands in the Lewis-acids and in the adducts almost remain in the same region. This indicates that the parent structure of the Lewis-acid is not disturbed and only pyridine is linked to M(M = Co(II) or Ni(II)). The coordination of pyridine to M is further supported by the fact that organomercury compounds have little tendency to act as Lewis-acid [8], hence there is a better chance of pyridine to link cobalt.

Cationic-Anionic Complexes: [M(bipy)$_3$][RHg(SCN)(SeCN)]$_2$

These complexes are soluble in Me_2SO and have been crystallized from this solvent. Their molar conductance data (123–145 cm^{-1} mhos/mol) in dimethylformamide indicate that they are 1:2 electrolytes. The electronic spectra and their spectral parameter and magnetic moment values show that Co(II) and Ni(II) have octahedral coordination geometry. They are more stable than the pyridine adducts and their decomposition into free selenium metal is very slow. The infrared spectra of the complexes show the absence of bands assigned to bridging selenocyanate and N-bonded thiocyanate [9]. In ν(CN) region bands are observed at 2100 cm^{-1} and 2120 cm^{-1}, which can be assigned to S-bonded thiocyanate and Se-bonded selenocyanate [10, 11]. The position of bands in ν(CS), ν(CSe), δ(NCSe), δ(NCS) regions also support bonding through 'S' or 'Se' ends. The number of bands in these regions indicate the presence of C_s symmetry, and existence of $[RHg(SCN)(SeCN)]^-$ ion. A band at about 245 cm^{-1} assigned to ν(ML) is present in all the cationic–anionic complexes. There is only one band in this region, which shows the presence of O_h symmetry and existence of $[M(L–L)_3]^{2+}$ cation.

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