Inorganica Chimica Acta, 83 (1984) L87–L91

Complexes of Ni/Hg Bimetallic Tetrathiocyanates with Chelating N,N′-Donors

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Received October 8, 1983

It is well known that polymeric bimetallic tetrathiocyanates of general formula $MM'(SCN)_4$ ($M = Mn^{II}, Fe^{II}, Co^{II}, Ni^{II}, Cu^{II}, Zn^{II}$; $M' = Zn^{II}, Cd^{II}, Hg^{II}, Pd^{II}$) react with different Lewis bases to form complexes in which the coordination numbers of M and M′ can be increased in relation to the original compounds. The different complex types and structures have recently been reviewed by Singh [1].

In addition to the monomeric bimetallic tetrathiocyanates with N-donor ligands, of general formula $L_4Ni(NCS)_2Hg(SCN_2)$ [2, 3], which contain terminal and bridging thiocyanate groups, two polymeric species types of general formula $>(SCN)_2NiL_2(NCS)_2Hg<$ [4–7] and $>(SCN)_2NiL_2(NCS)_2L_2Hg<$[3, 7] have been described in which only bridging thiocyanate groups are present. In all the cases peviously mentioned, the N-donor L ligands are monodentate. With bidentate N,N-donor ligands only a complex type $[Ni(L\text{–}L)_3][Hg(SCN)_4]$, derived from $NiHg(SCN)_4$ has been described [5].

In this work we study the formation of complexes derived from $NiHg(SCN)_4$ with the chelating N,N-donor ligands 2,2′-bipyridine (bipy), 1,10-phenanthroline (phen), 2,9-dimethyl-1,10-phenanthroline (dmp) and diacetyldihydrazone (ddh), using different preparative routes and molar ratios of reactants.

The infrared spectra, especially in the $\nu(C\equiv N)$ and $\nu(Ni\text{–}N)$ frequency regions, are important elements used in this study for determining bonding types. The metal isotope effect on metal–ligand vibrations [8] by changing Ni is used for the assignment of the $\nu(Ni\text{–}N)$ stretching frequencies. Electronic spectra and magnetic data have also been used in the study of the coordination environment of Ni^{II}.

Experimental

$NiCl_2\cdot6H_2O$ (Carlo Erba), $Hg(SCN)_2$ (Merck), 2,2′-bipyridine (Merck), 1,10-phenanthroline (Scharlau) and 2,9-dimethyl-1,10-phenanthroline (Merck) were commercially available.

$Ni(SCN)_2(NH_3)_4$ and diacetyldihydrazone were prepared as described by Grossmann [9] and Bayer [10] respectively.

^{62}Ni (99.32%) was supplied by the Electromagnetic Separation Groups, Chemistry Division, A.E.R.E. HARWELL.

General Method of Preparation

A solution of $NiCl_2\cdot6H_2O$ or $Ni(SCN)_2(NH_3)_4$ in a small amount of pure ethanol was added to a solution of the required amount of $Hg(SCN)_2$ in the same solvent. After 6 h stirring, a solution of the ligand in pure ethanol was added to the suspension previously formed, using the amount of ligand required for the desired complex. After 24 h stirring the coloured precipitate was filtered off, washed with ethanol and ether and dried in vacuum.

38 mg of ^{62}Ni treated with HCl (Merck) provided $^{62}NiCl_2\cdot6H_2O$ in sufficient yield for preparing the required amount of complex for the I.R. study. Only marked complexes which can be obtained from $NiCl_2\cdot6H_2O$ were prepared.

Analyses and Physical Measurements

C, H, N analyses were carried out by the Elemental Micro-Analysis Limited Laboratories, Amberley, Beaworthy (Devon), England. Ni and Hg were analyzed by Atomic Absorption Spectrometry, using a Perkin-Elmer 303 spectrophotometer.

Conductance measurements were performed in DMSO or DMFA at room temperature with a Philips conductivity bridge, Model No. CM 4144/01 and a PR 9512/00 cell. Infrared spectra in the 4000–350 cm^{-1} range were recorded as KBr disks on a Perkin-Elmer 325 spectrophotometer. The low-frequency I.R. spectra (350–200 cm^{-1}) were recorded on the same spectrophotometer, as concentrated Nujol mulls or polyethylene disks at a scanning rate of 2–4 mm/cm^{-1} and with a direct reading of the wavenumbers on the apparatus, the reproducibility on an average of three measurements being ±0.5 cm^{-1}. Electronic spectra were recorded on a Kontron Uvikon 820 spectrophotometer fitted with an integrating sphere 91-00247. $BaSO_4$ was used as reference substance for the diffuse reflectance spectra. Magnetic susceptibility measurements at temperatures between 77 K and 300 K were performed with a conventional Gouy system fitted with a Leybold VNK 3-300 cryo-evaporator.

Results and Discussion

Table I lists the analytical results and physical data of the isolated complexes.

0020-1693/84/$3.00

TABLE I. Analytical and Physical Data.

Complexes	Colour	Analyses, determined %				Magnetic data		Λ_M (ohm^{-1} cm^2 mol^{-1})	
		C	H	N	Ni	μ_{eff} (B.M.)	θ (K)	DMSO	DMFA
$(bipy)Ni(NCS)_2Hg(SCN)_2$	pale violet	27.97	1.23	12.97	8.90	2.67(28 ℃), 2.74(206 K)	−20	83.60	86.40
		(28.07)	(1.38)	(12.99)	(9.10)	2.79(151 K), 2.67(77 K)			
$(bipy)_2Ni(NCS)_2Hg(SCN)_2$	pale violet	35.48	1.97	13.39	7.00	3.21(24 ℃), 2.99(206 K)	−35	82.00	89.20
		(35.26)	(1.95)	(13.01)	(7.30)	2.98(151 K), 2.84(77 K)			
$[Ni(bipy)_3][Hg(SCN)_4]$	pale violet	42.87	2.47	14.82	6.00	3.06(25 ℃), 2.91(206 K)	−26	145.06	250.40
		(42.50)	(2.50)	(14.58)	(6.11)	2.89(151 K), 2.81(77 K)			
$(phen)Ni(NCS)_2Hg(SCN)_2$	pink	28.34	1.07	12.36	9.40	2.98(24 ℃), 2.85(206 K)	−24	56.56	81.20
		(28.71)	(1.16)	(12.18)	(8.70)	2.84(151 K), 2.73 (77 K)			
$(phen)_2Ni(NCS)_2Hg(SCN)_2$	pink-violet	37.58	1.86	12.11	7.10	3.41(24 ℃), 3.16(206 K)	−52	44.56	64.40
		(37.57)	(1.78)	(12.11)	(6.90)	3.12(151 K), 288(77 K)			
$[Ni(phen)_3][Hg(SCN)_4]$	pink-violet	45.20	2.23	13.50	5.15	3.90(25 ℃), 3.65(206 K)	−100	108.08	144.80
		(45.00)	(2.24)	(13.10)	(5.40)	3.50(151 K)			
$(dmp)Ni(NCS)_2Hg(SCN)_2$	light blue	30.54	1.79	12.01	8.71	3.24(24 ℃), 3.12(206 K)	−33	75.04	80.00
		(30.88)	(1.70)	(12.01)	(8.42)	3.10(151 K)			
$(dmp)_2Ni(NCS)_2Hg(SCN)_2$	light blue	41.99	2.76	12.11	6.28	3.37(24 ℃), 3.28(206 K)	−47	79.20	91.20
		(42.30)	(2.64)	(12.34)	(6.34)	3.15(151 K)			
$(dmp)_2NiHg(SCN)_2Cl_2$	light blue	39.70	2.72	9.74	6.30	2.54(24 ℃), 2.50(206 K)	−25	36.06	52.00
		(39.72)	(2.39)	(9.80)	(6.66)	2.45(151 K)			
$[Ni(dmp)_3][Hg(SCN)_4]$	light blue	49.78	3.16	12.56	4.96	3.54(24 ℃), 3.40(206 K)	−36	104.88	131.44
		(49.46)	(3.20)	(12.54)	(5.13)	3.30(151 K), 3.15(77 K)			
$[NiHg(SCN)_4]_3 2ddh \cdot 2NH_3$	pink-violet	13.68	1.96	17.71	9.09	3.11(24 ℃), 2.99(260 K)	−29	138.40	150.60
		(13.83)	(1.51)	(17.74)	(9.75)	2.94(151 K), 2.81(77 K)			
$(ddh)_2Ni(NCS)_2Hg(SCN)_2$	pink-violet	20.28	2.64	22.60	9.88	3.09(25 ℃), 2.98(206 K)	−20	42.16	70.64
		(20.00)	(2.78)	(23.35)	10.21)	2.95(151 K), 2.89(77 K)			
$(ddh)_2NiHg(SCN)_2Cl_2$	pink-violet	17.71	3.07	21.83	8.53	2.98(25 ℃), 2.88(206 K)	−39	32.03	50.00
		(17.82)	(2.99)	(22.12)	(8.70)	2.82(77 K)			
$[Ni(ddh)_3][Hg(SCN)_4]$	pink-violet	22.71	3.47	26.40	7.00	3.13(25 ℃), 3.09(206 K)	−19	125.36	134.40
		(23.00)	(3.60)	(26.88)	(7.00)	3.04(151 K)			

In the reactions with bipy and phen in molar ratio Ni/ligand 1:1, 1:2 and 1:3 the composition of the complexes isolated corresponds to the molar ratio of the reaction, independently of the starting compound used, $NiCl_2 \cdot 6H_2O$ or $Ni(SCN)_2(NH_3)_4$. In the reactions of $NiCl_2 \cdot 6H_2O$ with dmp and ddh, complexes of composition $NiHg(SCN)_2Cl_2(L-L)_2$ are formed for a molar ratio 1:2 (Ni/ligand) or higher. The reaction in molar ratio 1:1 results in no definite products. However the reactions from $Ni(SCN)_2(NH_3)_4$ always yields compounds whose composition corresponds to the molar ratio 1:1. In this case, a compound of empirical formula $[NiHg(SCN)_4]_3 \cdot 2ddh \cdot 2NH_3$ is formed, which can be considered as similar to the 1:1 complexes of the remaining ligands, 1/3 of the bidentate ddh molecules being substituted by the stoichiometric amount of monodentate molecules NH_3.

All these compounds are microcrystalline solids, insoluble in the organic solvents of medium polarity and soluble in DMSO and DMF. They decompose without melting between 180 and 210 °C. The molar conductivity values of the 1:1 and 1:2 complexes in DMSO and DMF are lower than those corresponding to 1:1 electrolytes, but higher than those of typical non-electrolytes. This fact could indicate an interaction with the solvent which leads to formation of ionic species. However the conductivity values of the 1:3 complexes correspond to typical 2:2 electrolytes and these complexes can be formulated as cationic–anionic species $[Ni(L-L)_3][Hg(SCN)_4]$.

The ligand-field transitions observed in the reflectance spectra can be interpreted in all cases by referring to the energy level diagram for octahedral d^8 ions. In the $(bipy)_nNiHg(SCN)_4$ complexes, a displacement of ν_1 (11.000–12.700 cm^{-1}) towards the higher energy values with increasing number of bipy ligands was observed which can be explained on the basis of the stronger donor nature of the bipy ligands with respect to that of isothiocyanate. In the spectra of $(ddh)_2Ni(NCS)_2Hg(SCN)_2$ and $(ddh)_2NiHg(SCN)_2Cl_2$ two bands of approximately the same intensity was observed between 11.100 and 12.900 cm^{-1}, which could be due to a tetragonal splitting of the ν_1 band.

The reciprocal mol-susceptibility; $1/\chi'_M$, of all these complexes varies linearly with the temperature, and the θ values can be used as an indication of the extent of increase of μ_{eff} with temperature. The magnetic moments (Table I) at room temperature fall in the usual range for six-coordinate Ni^{II} ions, except in the case of $(dmp)_2NiHg(SCN)_2Cl_2$, in which μ_{eff} = 2.54 B.M. This fact can be due to the mixing of a low-spin state, which is possible for a trans-octahedral configuration with a weak tetragonal field. In this case μ_{eff} should depend on the thermal population of a low-lying paramagnetic level ^3B separated from the ^1A ground state by a small gap [11]. Magnetic moments lower than the spin-only value for a high-spin d^8 configuration have also been observed for $(bipy)NiHg(SCN)_4$ and $(phen)NiHg(SCN)_4$ at low temperatures. The magnetic moments of $(L-L)_2NiHg(SCN)_4$ complexes (L–L = phen, dmp) may correspond to tetragonal six-coordinated species [12].

In relation to ligand vibrations in the 4000–350 cm^{-1} region, the complexes with bipy, phen and dmp show the shifts and splittings characteristic of the coordinated ligands [13, 14]. In the complexes with ddh, the ν(C=N) stretching vibrations of the hydrazone groups appear shifted towards higher frequencies, as occurs with other complexes of this ligand [15, 16].

The I.R. frequencies which provide most information about the bonding type are those corresponding to the ν(C≡N) stretching vibrations of the thiocyanate groups. The complexes of composition $(L-L)NiHg(SCN)_4$ (L–L = bipy, phen) show a band with two maxima, which correspond to ν(C≡N) bridging thiocyanate groups. This fact, together with the six-coordination of Ni^{II} deduced earlier, suggests a polymeric structure for these complexes. The thiocyanate bands observed for $(dmp)NiHg(SCN)_4$ are similar to those of the corresponding complexes of bipy and phen, but in this case, two weak bands appearing in the ν(C≡N) region of terminal thiocyanate groups might be due to polymers shorter than those of the above mentioned complexes, which should increase the number of terminal thiocyanates at the ends of the polymeric units.

In the complexes of composition $(L-L)_2NiHg(SCN)_4$ (L–L = bipy, phen, dmp, ddh) and $[NiHg(SCN)_4]_3 \cdot 2ddh \cdot 2NH_3$ bands assignable to ν(C≡N) of terminal and bridging thiocyanate groups are observed, whereas in the complexes of composition $[Ni(L-L)_3][Hg(SCN)_4]$ and $(L-L)_2NiHg(SCN)_2Cl_2$ (L–L = dmp, ddh) only bands corresponding to terminal mercury-bonded groups are present [17].

The assignments of the metal–ligand vibrations in the 350–200 cm^{-1} region were made by the isotopic displacement method. The metal–ligand stretching frequencies show isotopical shifts ($\Delta\bar{\nu}$ = 2–6 cm^{-1}) if the metal is isotopically substituted [8, 18–20], whereas the ligand bands activated by coordination [8, 21, 22] appearing in the same spectral region remain at the same frequency values in the marked compounds. Table II shows the assignments of the ν(Ni–N) stretching frequencies together with the corresponding isotopical shifts ($\Delta\bar{\nu}$). The Ni natural isotopical mixture and ^{62}Ni (99.22%) were used for the preparation of the samples studied here. Only the ^{62}Ni complexes which can be obtained in high yield from $NiCl_2 \cdot 6H_2O$ were prepared.

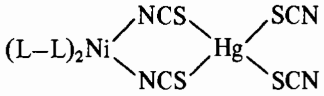
TABLE II. Infrared Spectra in the 350–200 cm^{-1} Region.

Complexes	ν(Ni–N$_L$)	$\Delta\bar{\nu}$	ν(Ni–NCS)	$\Delta\bar{\nu}$	ν(Hg–S)	Activated ligand bands
(bipy)Ni(NCS)$_2$Hg(SCN)$_2$	285m	8	230s	4	205w	278s(C)250m(D)
	262m	9	224s	2		213sh(E)
(bipy)$_2$Ni(NCS)$_2$Hg(SCN)$_2$	287s	5	230w	4		292h(C)246h(D)
	273s	5	224m	4		
[Ni(bipy)$_3$] [Hg(SCN)$_4$]	280s				208m	292sh(C)235sh(D)
	255m					213sh(E)
(phen)Ni(NCS)$_2$Hg(SCN)$_2$	301s	4	230w	4	210w	308sh(B)256sh(C)
	253s	5	225s	4		241sh(C)
(phen)$_2$Ni(NCS)$_2$Hg(SCN)$_2$	300s	4	243m	7	210s	307sh(B)268m(C)
	253mbr	6	228sh	6		
[Ni(phen)$_3$] [Hg(SCN)$_4$]	298s				210w	303sh(B)264sh(C)
	254sh					
	245m					
(dmp)Ni(NCS)$_2$Hg(SCN)$_2$	269m		238m		218m	336m(B)285m(B)
	265m		229sh			250w(C)
(dmp)$_2$Ni(NCS)$_2$Hg(SCN)$_2$	274s		234m		212w	338m(B)287m(B)
	258sbr		220sh			250w(C)
(dmp)$_2$NiHg(SCN)$_2$Cl$_2$	270s				210w	336sh(B)285m(B)
	262sbr					255sh(C)
[Ni(dmp)$_3$] [Hg(SCN)$_4$]	268s				210w	336m(B)286m(B)
	258s					
[NiHg(SCN)$_4$]$_3$2ddh·2NH$_3$	270sh		255m		205sh	350w, 305m
	266m					218mbr
(ddh)$_2$Ni(NCS)$_2$Hg(SCN)$_2$	273m		258m		205w	350w, 306m
			250sh			220m
(ddh)$_2$NiHg(SCN)$_2$Cl$_2$	270w		258m		210w	350w, 304m
						230w
[Ni(ddh)$_3$] [Hg(SCN)$_4$]	272w				210w	350w, 303m
	269sh					228w

The spectra of the (L–L)NiHg(SCN)$_4$ complexes show two bands at 270–243 cm^{-1}, which shift towards lower frequencies ($\Delta\bar{\nu}$ = 4–8 cm^{-1}) in the marked compounds and were assigned to ν(Ni–N$_L$) stretching frequencies. The same complexes show two other bands at 240–255 cm^{-1} which are sensitive to the isotopic substitution ($\Delta\bar{\nu}$ = 4–6 cm^{-1}) and have been assigned to ν(Ni–NCS) stretching frequencies. Bands assignable to ν(Ni–NCS) stretching frequencies cannot be observed in the spectra of 1:3 complexes, which confirms their ionic nature. It should be noted that ν(Ni–N$_L$) and ν(Ni–NCS) are rather similar in complexes with the same ligand but different composition, and only a small lowering in the ν(Ni–N$_L$) frequencies with increasing number of bidentate ligands can be observed. This fact could be due to the general six-coordination of Ni^{II} in these complexes. The ν(Ni–N$_L$) frequencies measured in the [Ni(L–L)$_3$] [Hg(SCN)$_4$] complexes (L–L = bipy, phen) are similar to those given by Hutchinson *et al.* [21] for other salts of these cationic complexes.

On the basis of all these studies, we can assume that the 1:1 complexes are polymeric species in which the Ni^{II} ions are octahedrally coordinated to the nitrogen atoms of one N,N-ligand and four thiocyanate groups, whereas the Hg ions are tetrahedrally coordinated to four sulfur atoms of thiocyanate groups, these polymers being similar to those proposed in the literature for (SCN)$_2$NiL$_2$-(NCS)$_2$Hg complexes [4–7], but of *cis*-configuration. The complex formulated as [NiHg(SCN)$_4$]·2ddh·2NH$_3$ can also be considered as a 1:1 complex, but with shorter polymeric chains, which makes possible the presence of some terminal thiocyanate groups.

The 1:2 complexes contain octahedral or pseudooctahedral Ni^{II} species in which the Ni^{II} ions are coordinated to nitrogen atoms of two bidentate N,N-ligands and two thiocyanate groups. Molecular monomeric cis-species (a) or polymeric trans-species (b) containing terminal and bridging thiocyanate groups are possible, the polymeric trans-species being more probable for L–L = phen, dmp and ddh. The monomeric species are similar to the L$_4$Ni(NCS)Hg(SCN)$_2$ complexes described in the literature [2,3].



(a)

$-SCN-Ni(L-L)_2-NCS-Hg(SCN)_2-$

(b)

The 1:2 complexes of composition $(L-L)_2NiHg(SCN)_2Cl_2$ (L–L = dmp, ddh) also contain octahedral Ni^{II} species in which Ni^{II} is coordinated to four nitrogen atoms of two bidentate ligands, the remaining coordination sites being occupied by chloro bridging ligands and Hg^{II} is tetrahedrally coordinated to two bridging chloro ligands and two terminal thiocyanate groups. The electronic spectra and magnetic moments seem to be indicative of a trans-octahedral coordination of Ni^{II} and, consequently, of a polymeric structure $-Cl-Ni(L-L)_2-Cl-Hg(SCH)_2-$. The 1:3 complexes are ionic species $[Ni(L-L)_3][Hg(SCN)_4]$.

Acknowledgement

Financial support from the Comisión Asesora de Investigación Científica y Técnica (Project No.: 3727-79) for this work is gratefully acknowledged.

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