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# Complexes of Zn/Hg Bimetallic Tetrathiocyanates with Chelating N,N'-Donors

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*Bimetallic Zn/Hg tetrathiocyanate complexes with N,N'-chelating ligands of general formula* $(L-L)_n$-$Zn(NCS)_2Hg(SCN)_2$ *(n = 1, 2; L–L = 2,2'-bipyridine, 1,10-phenanthroline, 2,9-dimethyl-1,10-phenanthroline) were prepared from* $ZnCl_2$ *or* $Zn(SCN)_2$ *by reaction with the corresponding stoichiometrical amounts of* $Hg(SCN)_2$ *and ligand. Only a complex of composition* $[Zn(L-L)_3][Hg(SCN)_4]$ *could be isolated from the reactions in molar ratio 1:3 Zn/ligand for L–L = 1,10-phenanthroline. The reaction from* $ZnCl_2$ *with diacetyldihydrazone in molar ratios 1:2 or more affords a single complex of composition* $(L-L)Zn(NCS)_2Cl_2Hg$ *and the reaction from* $Zn(SCN)_2$ *in molar ratios 1:2 or more gives only a complex of composition* $(L-L)Zn(NCS)_2Hg(SCN)_2$*. The complexes were studied by elemental analysis, conductance measurements and infrared spectroscopy. An infrared study in the low-frequency region was made by the isotopical substitution method, using* $^{68}Zn$ *marked complexes.*

## Introduction

It is well known that the 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 made to rise with respect to the original compounds. The different complex types and structures have been recently reviewed by Singh [1].

Only one type of Zn/Hg bimetallic tetrathiocyanato complex of general formula $L_2Zn(NCS)_2$-$Hg(SCN)_2$ (L = pyridine, thiohydantoine, ethylenethiourea, thiazolhydantoine, pyrazine-2,3-dicarboxamide, isonicotinic acid hydrazide) has been described [2–5], in which both metallic ions are four-coordinated.

In this work we study the possibility of formation of complexes containing six-coordinated Zn(II) ions derived from $ZnHg(SCN)_4$ with the chelating ligands, 2,2'-bipyridine (bipy), 1,10-phenanthroline (phen), 2,9-dimethyl-1,10-phenanthroline (DMP) and diacethyldihydrazone (DDH), using different preparative routes and molar ratios of reactants.

The infrared spectra, especially in the $\nu(C{\equiv}N)$ and $\nu(Zn-N)$ frequency regions, are the principal diagnosis of bonding in this study. The metal isotope effect on metal–ligand vibrations [6] by changing of Zn is used for the assignment of the $\nu(Zn-N)$ stretching frequencies.

## Results and Discussion

In the reactions with bipy, phen and DMP in molar ratio Zn/ligand 1:1 and 1:2 the composition of the complexes obtained corresponds to the molar ratio employed. The use of $ZnCl_2$ or $Zn(SCN)_2$ in the reaction affords the same results. The reactions in molar ratio 1:3 with these ligands yield a 1:3 complex only in the case of the phenanthroline ligand.

In the reactions with DDH from $ZnCl_2$ as starting compound no definite complex was formed for the 1:1 Zn/DDH molar ratio and the reaction in molar ratio 1:2 leads to the formation of $ZnHgCl_2(NCS)_2$-(DDH). $ZnHg(SCN)_4(DDH)_2$ is formed only in reactions from $Zn(NCS)_2$ when the molar ratio Zn/DDH is 1:2 or more.

In all cases the solubility of the different complexes seems to determine the stoichiometry of the reactions.

The complexes obtained are white, microcrystalline solids, insoluble in the organic solvents of medium polarity and soluble in DMSO and DMF. The 1:1 and 1:2 complexes are non-electrolyte in DMF, but the 1:3 phenanthroline complex behaves as an ionic compound. It was not possible to obtain crystals of these solids adequate for structure determinations. Table I lists the analytical results and physical data of all these complexes.

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TABLE I. Analytical and Physical Data.

| Complexes | %C | | %H | | %N | | %Zn | | Molar. Cond. ($\Omega^{-1}$ cm$^2$ mol$^{-1}$) | | D.T.* (°C) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | Calcd. | Found | Calcd. | Found | Calcd. | Found | Calcd. | Found | DMSO | DMF | |
| (bipy)Zn(NCS)$_2$Hg(SCN)$_2$ | 25.70 | 25.79 | 1.22 | 1.29 | 12.85 | 12.84 | 9.95 | 9.16 | 29.69 | 26.58 | 210–275 |
| (bipy)$_2$Zn(NCS)$_2$Hg(SCN)$_2$ | 35.57 | 35.76 | 1.98 | 1.90 | 13.83 | 13.81 | 8.58 | 9.80 | 44.56 | 47.30 | 210–275 |
| (phen)Zn(NCS)$_2$Hg(SCN)$_2$ | 27.58 | 27.51 | 1.14 | 1.31 | 12.06 | 12.44 | 9.34 | 8.83 | 36.70 | 36.95 | 210–275 |
| (phen)$_2$Zn(NCS)$_2$Hg(SCN)$_2$ | 37.57 | 37.62 | 1.79 | 1.96 | 12.58 | 12.82 | 7.35 | 7.08 | 37.87 | 47.34 | 210–275 |
| [(phen)$_3$Zn] [Hg(SCN)$_4$] | 43.93 | 44.50 | 2.19 | 2.20 | 12.81 | 13.03 | 5.95 | 5.40 | 105.20 | 110.40 | 220–270 |
| (DMP)Zn(NCS)$_2$Hg(SCN)$_2$ | 30.20 | 30.60 | 1.67 | 1.70 | 11.74 | 11.74 | 9.10 | 9.00 | 39.14 | 40.95 | 210–270 |
| (DMP)$_2$Zn(NCS)$_2$Hg(SCN)$_2$ | 41.18 | 41.27 | 2.57 | 2.55 | 12.01 | 12.57 | 7.87 | 8.00 | 44.35 | 48.70 | 210–270 |
| (DDH)Zn(SCN)$_2$Cl$_2$Hg | 12.71 | 12.74 | 1.76 | 1.66 | 14.83 | 14.83 | 11.47 | 11.12 | 40.11 | 42.30 | 210–270 |
| (DDH)$_2$Zn(NCS)$_2$Hg(SCN)$_2$ | 19.86 | 20.08 | 2.75 | 2.65 | 23.17 | 22.81 | 8.96 | 8.60 | 43.21 | 44.80 | 210–270 |

*Decomposition temperature range. The complexes decompose without melting.

Table II gives the most significant infrared frequencies in the 4000–350 cm$^{-1}$ region for the different complexes. In relation with the ligand vibrations, the complexes with bipy, phen and DMP show the shifts and splittings characteristic of the coordinated ligands [7, 8]. In the complexes with DDH, the $\nu$(C=N) stretching vibrations of the hydrazone groups appear displaced towards the higher frequency values, as occurs with other complexes of this ligand [9, 10].

The I.R. frequencies which afford most information about the bonding type are those corresponding to the $\nu$(C≡N) stretching vibrations of the thiocyanate groups. The complexes of composition ZnHg(SCN)$_4$(L–L) (L–L = bipy, phen, DMP) shows a structured band with two maxima at higher frequency values, which can be undoubtedly assigned to $\nu$(C≡N) of bridging thiocyanate groups and two (or three) maxima at lower frequency values, which can be assigned to $\nu$(C≡N) of mercury-bonded thiocyanate groups. The spectra of the ZnHg(SCN)$_4$(L–L)$_2$ complexes in the thiocyanate region are quite similar, but the $\nu$(C≡N) stretching frequencies appear slightly displaced towards the lower values with respect to the 1:1 complexes. No $\nu$(C≡N) bridging thiocyanate bands were observed in the spectrum of ZnHg(SCN)$_4$(phen)$_3$, which renders the ionic formula [Zn(phen)$_3$] [Hg(SCN$_4$] highly probable for this complex. (DDH)Zn(SCN)$_2$Cl$_2$Hg also shows two bands corresponding to $\nu$(C≡N) of bridging thiocyanate groups.

Only in the DDH complexes could the $\nu$(C=S) stretching frequencies of the thiocyanate groups be observed, owing to the presence of numerous strong aromatic ring bands of the ligands in the spectra of the remaining complexes [8].

The assignments of the metal–ligand vibrations in the region 350–200 cm$^{-1}$ 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 [6, 11–13] whereas the ligand bands activated by coordination [14–16] appearing in the same spectral region remain at the same frequency values. Table III shows the assignments of the $\nu$(Zn–N) stretching-frequencies together with the corresponding isotopical shifts ($\Delta\bar{\nu}$). The Zn natural isotopic mixture and $^{68}$Zn (97.91%) were used for the preparation of the samples studied here. Only the $^{68}$Zn complexes which can be obtained from ZnCl$_2$ were prepared.

The spectra of the ZnHg(SCN)$_4$(L–L) complexes show two bands at 284–269 cm$^{-1}$, which shift towards the lower frequencies ($\Delta\bar{\nu}$ = 2.4 cm$^{-1}$) in the marked compounds. These bands, in accordance with assignments in the literature for similar compounds [1, 2, 5], were assigned to $\nu$(Zn–NCS) stretching vibrations. The same complexes show two other bands at 245–215 cm$^{-1}$ which are sensitive

TABLE II. The Most Significant Infrared Frequencies in the 4000–350 cm$^{-1}$ Region.

| Complexes | $\nu$(C≡N)$_{bri}$ | $\nu$(C≡N)$_{ter}$ | $\delta$(SCN) | $\nu$(C=S) | $\nu$(C=N) |
|---|---|---|---|---|---|
| (bipy)Zn(NCS)$_2$Hg(SCN)$_2$ | 2160vs | 2120s | 470s | | |
| | 2135sh | 2080m | 455m | | |
| | | | 446m | | |
| (bipy)$_2$Zn(NCS)$_2$Hg(SCN)$_2$ | 2147sh | 2110s | 470m | | |
| | 2130vs | 2075sh | 456s | | |
| | | | 447s | | |
| | | | 434m | | |
| (phen)Zn(NCS)$_2$Hg(SCN)$_2$ | 2160s | 2090m | 470m | | |
| | 2140m | 2075m | 466m | | |
| | | | 455w | | |
| | | | 446s | | |
| (phen)$_2$Zn(NCS)$_2$Hg(SCN)$_2$ | 2130m | 2083m | 464m | | |
| | 2115s | 2070s | 447m | | |
| | | | 437w | | |
| | | | 427w | | |
| [(phen)$_3$Zn] [Hg(SCN)$_4$] | | 2110m | 478m | | |
| | | 2080s | 465m | | |
| | | 2060s | 442m | | |
| | | | 437sh | | |
| (DMP)Zn(NCS)$_2$Hg(SCN)$_2$ | 2160s | 2118w | 472m | | |
| | 2130w | 2095s | 448m | | |
| | | 2080s | 438m | | |
| (DMP)$_2$Zn(NCS)$_2$Hg(SCN)$_2$ | 2154m | 2113m | 480m | | |
| | 2127s | 2075s | 452w | | |
| | | 2052s | 444w | | |
| | | | 436m | | |
| (DDH)Zn(NCS)$_2$Cl$_2$Hg | 2159vs | | 468m | 774w | 1610m,br |
| | 2142m | | 453sh | | |
| | 2126sh | | 445m | 702w | |
| (DDH)$_2$Zn(NCS)$_2$Hg(SCN)$_2$ | 2145w | 2111s | 472m | 775w | 1610s |
| | 2128s | 2075sh | 465m | 703w | |
| | | | 458m | | |
| | | | 438m | | |

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

| Complexes | $\nu$(Zn–NCS) | $\Delta\bar{\nu}^*$ | $\nu$(Zn–N$_L$) | $\Delta\bar{\nu}^*$ | $\nu$(Hg–S) | Activated ligand bands |
|---|---|---|---|---|---|---|
| (bipy)Zn(NCS)$_2$Hg(SCN)$_2$ | 274s | 3.0 | 232m | 6.0 | | 304w(B), 290w, 283m(C) |
| | 269s | 3.0 | 220sh | 6.0 | 206w | 263w(D), 241sh(E) |
| (bipy)$_2$Zn(NCS)$_2$Hg(SCN)$_2$ | 272s | 4.0 | 230 | 7.0 | | 303w(B), 290w, 282w(C) |
| | 268s | 4.0 | 222 | 7.0 | 210w | 261w(D), 245w(E) |
| (phen)Zn(NCS)$_2$Hg(SCN)$_2$ | 284s | 2.0 | 242m | 2.0 | | 305w(B), 252w(C), 248w(C) |
| | 274s | 4.0 | 220m | 5.0 | 208w | |
| (phen)$_2$Zn(NCS)$_2$Hg(SCN)$_2$ | 284m | 2.0 | 241m | 3.0 | | 304w(B), 253w(C), 248w(C) |
| | 271s | 3.0 | 227w | 4.0 | 207w | |
| [(phen)$_3$Zn] [Hg(SCN)$_4$] | | | 235w | | 210m | 304w(B), 262m(C), 250m(C) |
| | | | 222m | | 206w | |
| (DMP)Zn(NCS)$_2$Hg(SCN)$_2$ | 275s | 4.0 | 235w | 5.0 | | 304w(B), 292w(B), 284w(B) |
| | 269s | 3.0 | 219m | 5.0 | 210w | 263w(C), 250w(C) |
| (DMP)$_2$Zn(NCS)$_2$Hg(SCN)$_2$ | 274s,br | 4.0 | 232w | 4.0 | | 305w(B), 291w(B), 284w(B) |
| | | | 218m | 2.0 | 208w | 263w(C), 250w(C) |

*(continued overleaf)*

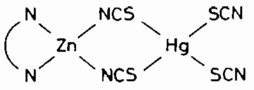
TABLE III. *(continued)*

| Complexes | $\nu$(Zn–NCS) | $\Delta\bar{\nu}$* | $\nu$(Zn–N$_L$) | $\Delta\bar{\nu}$* | $\nu$(Hg–S) | Activated ligand bands |
|---|---|---|---|---|---|---|
| (DDH)Zn(NCS)$_2$Cl$_2$Hg | 275s | | 250w | | | 299w, |
| | 264w | | 247w | | | |
| (DDH)$_2$Zn(NCS)$_2$Hg(SCN)$_2$ | 280s | | 240w | | | 216m |
| | 270s | | 234m | | 208w | |

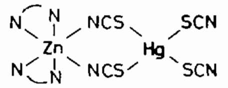
*$\Delta\bar{\nu}$ indicates metal isotope shift, $\bar{\nu}(^{64}$Zn$) - \bar{\nu}(^{68}$Zn$)$.

to the isotopical substitution ($\Delta\bar{\nu}$ = 6–7 cm$^{-1}$) and have been assigned to $\nu$(Zn–N$_L$) stretching frequencies. The spectral ranges at which the $\nu$(Zn–NCS) and $\nu$(Zn–N$_L$) stretching frequencies appear in the ZnHg(SCN)$_4$(L–L)$_2$ complexes are surprisingly similar to those of the corresponding 1:1 complexes. The presence of ligand bands activated by complexation in the same spectral region, which are stronger than in the corresponding 1:1 complexes, makes it sometimes difficult to observe the $\nu$(Zn–N$_L$) bands; however, a careful comparison of the normal and marked complex spectra makes their assignments possible. It is to be noted that the isotopical shifts, $\Delta\bar{\nu}$, are greater for the $\nu$(Zn–NCS) stretching vibrations.

On the basis of the infrared study in the thiocyanate $\nu$(C≡N) stretching frequency region, we suppose that the ZnHg(SCN)$_4$(L–L)$_n$ (n = 1, 2) complexes are probably molecular species with the following tentative structural formulae:



( N-N = bipy, phen, DMP )



( N-N = bipy, phen, DMP, DDH )

The similarity of the $\nu$(Zn–N) stretching frequencies in the 1:1 and 1:2 complexes could be explained if the expected releasing of the Zn–N bonds, caused by the increase in the coordination number of Zn in the 1:2 complexes, were compensated by a reinforcement of these bonds by a $\pi$ back-bonding to both thiocyanate and L–L ligands. This could explain also the lower $\nu$(C≡N) frequencies of the bridging thiocyanate groups in the 1:2 complexes.

(DDH)Zn(NCS)$_2$Cl$_2$Hg is probably a polymeric complex with bridging chloride and thiocyanate groups on the basis of the absence of bands assignable to $\nu$(Hg–Cl) stretching frequencies and the presence of $\nu$(C≡N) bands only in the range corresponding to bridging thiocyanate groups. In the low-frequency region strong bands at 275 and 264 cm$^{-1}$ appear which were assigned to $\nu$(Zn–NCS) stretching frequencies. The weak bands at 250 and 247 cm$^{-1}$ were assigned to $\nu$(Zn–N$_L$).

In the spectrum of [Zn(phen)$_3$][Hg(SCN)$_4$] no bands assignable to $\nu$(Zn–NCS) stretching vibrations were observed. Two bands at 235 and 222 cm$^{-1}$ were assigned to $\nu$(Zn–N$_L$) stretching vibrations.

$\nu$(Hg–S) appears in all these compounds as a medium or weak band in the range 204–210 cm$^{-1}$, similar to those given in the literature for analogous compounds [2].

From the foregoing we conclude the existence of complexes containing chelating ligands derived from ZnHg(SCN)$_4$ in which the Zn(II) ions are six-coordinated. Two or three complexes of four- or six-coordination around the Zn(II) ions can be formed depending on the molar ratio Zn/ligand of the reaction.

## Experimental

ZnCl$_2$ (FEROSA), Hg(SCN)$_2$ (Merck), 2,2′-bipyridine (Merck), 1,10-phenanthroline (Scharlau) and 2,9-dimethyl-1,10-phenanthroline (Merck) of analytical grade were obtained commercially.

Zn(SCN)$_2$ and diacetyldihydrazone were prepared by methods described in the literature by Masaki [17] and Bock [18] respectively.

$^{68}$Zn (97.9%) was supplied by the Electromagnetic separation Groups, Chemistry Division, A.E.R.E., HARWELL.

### *General Method of Preparation*

A solution of ZnCl$_2$ or Zn(SCN)$_2$ in a minimum amount of absolute ethanol was added to a solution of the required amount of Hg(SCN)$_2$ in the same solvent. After 12 hr of stirring at room temperature, a solution of the ligand in the same solvent was added to the suspension formed, using the amount of ligand required for the desired complex, and the reaction mixture was stirred for 48 hr. A white, microcrystalline precipitate was formed, which was filtered off, washed with ethanol and ether and dried in a vacuum.

Identical products were isolated from the reactions of $ZnCl_2$ or $Zn(SCN)_2$ with bipy, phen and DMP as ligands, and therefore $ZnCl_2$ was used as reactant for the preparation of the $^{68}Zn$ complexes. 38 mg of $^{68}Zn$ treated with HCl (Merck) affords enough $^{68}ZnCl_2$ for the preparation of the amount of the complex required for the I.R. study.

### *Analyses and Physical Measurements*

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

Conductance measurements were performed in DMF at room temperature with a Philips conductivity bridge, Model No. CM 4144 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 (350–200 $cm^{-1}$) I.R. spectra were recorded on the same spectrophotometer, as Nujol mulls or polyethylene disks at a scanning rate of 2–4 $mm/cm^{-1}$ and with a direct reading of the wave-numbers on the apparatus, the reproducibility on an average of three measurements being $\pm 0.5$ $cm^{-1}$.

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