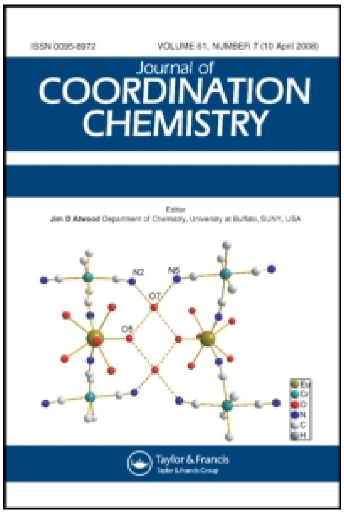

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# SYNTHESIS AND CHARACTERIZATION OF DINUCLEAR, BRIDGED COMPLEXES OF THE TYPE $L_xM(NCSe)_2M'(SCN)_2L'_2$

P. P. Singh[a]; A. K. Gupta[a]; A. K. Srivastava[a]
[a] Department of Chemistry, M.L.K. College, Balrampur, U.P., India

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# SYNTHESIS AND CHARACTERIZATION OF DINUCLEAR, BRIDGED COMPLEXES OF THE TYPE $L_xM(NCSe)_2M'(SCN)_2L'_2$

P. P. SINGH, A. K. GUPTA and A. K. SRIVASTAVA
*Department of Chemistry, M.L.K. College, Balrampur-271201, U.P. India*

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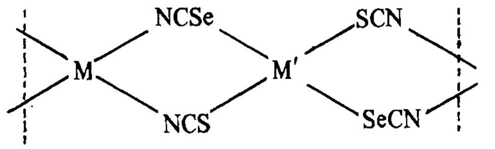
$L_xM(NCSe)_2M'(SCN)_2(PPh_3)_2$ [M = Co(II), Ni(II); M′ = Hg(II), Cd(II), Zn(II); L = pyridine (py), 2,2′-bipyridyl (bipy); $x$ = 4, 2] have been synthesized. Elemental analysis, magnetic moment, electronic and infrared spectral and thermogravimetric studies indicate that these complexes are dinuclear. The total softness of M and M′ in the complexed state have also been calculated to derive certain conclusions.

## INTRODUCTION

Bimetallic tetrathiocyanates and tetraselenocyanates $>M(NCX)_2M'(XCN)_2<$ (X = S, Se) have two points of unsaturation, one at M and the other at M′. The values of softness[1] as calculated from the Klopman equation for cobalt, nickel and mercury are −0.22, −0.52 and −4.87 respectively. The difference in their softness values indicates that the two metals will prefer different types of ligands. We synthesized complexes in which two different ligands are linked to the two different sites. To bring an additional novelty we have reacted a new type of mixed dithio diselenocyanate, the structure of which is as shown in the diagram below.



[M = Co(II), Ni(II), M′ = Hg, Cd, Zn]

## EXPERIMENTAL

### *Material and Manipulations*

All chemicals were reagent grade and were purified by known methods. KSeCN, $M(NCSe)_2$ [M = Co(II), Ni(II)] and $M'(SCN)_2$ [M′ = Hg(II), Cd(II), Zn(II)] were prepared and recrystallized by methods described elsewhere.[1,2]

### *Preparations of $(py)_4M(NCSe)_2M'(SCN)_2(PPh_3)_2$ and $(bipy)_2M(NCSe)_2M'(SCN)_2(PPh_3)_2$ [M = Co(II), Ni(II), M′ = Hg(II), Cd(II), Zn(II)]*

The complexes were prepared by the following three different methods.

1) 3.5 ml of pyridine was dissolved in 100 ml of methanol. To the solution 2.69 gms of $M(NCSe)_2$ was added and stirred for 2 h at room temperature. $M(NCSe)_2.4py$ appeared in the form of a precipitate. This precipitate was brought in solution by adding a mixture of 2 ml of pyridine in 50 ml of methanol. To this solution a suspension of 8.4 gms of $Hg(SCN)_2.2PPh_3$ or 7.52 gms of $Cd(SCN)_2.2PPh_3$ or 7.05 gms $Zn(SCN)_2.2PPh_3$ in 100 ml of methanol was added and stirred for 6 h at room temperature. Pink precipitates were formed in each case which were filtered, washed with the solvent and dried in vacuum. Bipyridyl complexes were similarly prepared, by starting with a solution of 3.2 gms of 2,2′-bipyridyl in 100 ml of methanol.

2) $M'(SeCN)_2.2PPh_3$, $M(NCS)_2.4py$ and $M(NCS)_2.2bipy$ were prepared by the direct action of ligands on the respective seleno- and thiocyanates. Solutions or suspensions of 9.34 gms of $Hg(SeCN)_2.2PPh_3$ or 8.46 gms of $Cd(SeCN)_2.2PPh_3$ or 7.99 gms of $Zn(SeCN)_2.2PPh_3$ and 4.91 gms of $M(NCS)_2.4py$ or 4.87 gms of $M(NCS)_2.2bipy$ in 100 ml methanol were mixed, 1 ml of pyridine or 0.5 gms of bipyridyl was added and stirred for 24 h at room temperature. Solid compounds were formed in each case, which were filtered, washed with solvents, and ether and dried in vacuum.

3) To a suspension of 4.97 gms of $\rangle M(NCS)(NCSe)Cd(SeCN)(SCN) \langle$ or 4.5 gms of $\rangle M(NCS)(NCSe)Zn(SeCN)(SCN) \langle$ in 100 ml of methanol, pyridine was added dropwise with continuous stirring till the complex dissolved. To this solution a solution of 5.3 gms of triphenylphosphine in 100 ml of methanol was added and stirred for 24 h at room temperature. A pink precipitate was formed in each case which was filtered, washed with solvent and dried in vacuum. Since $\rangle M(NCS)(NCSe)Hg(SeCN)(SCN) \langle$ was not soluble in pyridine, a suspension containing its 5.85 gms and 5 ml pyridine in 100 ml of methanol was stirred with 5.3 gms of triphenylphosphine in the same solvent. Bipyridyl complexes were similarly prepared by taking a concentrated solution of bipyridyl in methanol in place of pyridine.

$\rangle Co(NCS)(NCSe)M'(SeCN)(SCN) \langle$ was mixed with triphenylphosphine and stirred for 6 h. A green complex $(PPh_3)_2Co(NCSe)_2M'(SCN)_2$ was obtained. To the suspension of the complexes in methanol, excess pyridine or bipyridyl was added and stirred for 24 h. at room temperature. These bases did not react with $(PPh_3)_2Co(NCSe)_2M'(SCN)_2$.

### *Analysis of the complexes*

The complexes were analyzed for selenium as selenium metal, nickel as nickel dimethyl glyoximate, mercury as mercury sulphide and cobalt, cadmium and zinc as their anthranilates. Nitrogen was estimated by semimicro Kjeldahl method.[3] The analytical data, the m.p. and color of the complexes are presented in Table I.

### *Physical Measurements*

Infrared spectra in the range 4000–350 cm$^{-1}$ and 500–50 cm$^{-1}$ were recorded on Perkin Elmer model-521 and Polytech FIR-30 spectrophotometers, respectively. Spectra in the range 4000–350 cm$^{-1}$ were obtained as Nujol mulls and in 500–50 cm$^{-1}$ as polythene pellets. Electronic spectra of mulled solids were recorded on Carl Zeiss DMR-21 spectrophotometer between 1800–300 nm. The magnetic susceptibility measurements were made at room temperature by Gouy's method using cobalt mercury tetrathiocyanate as reference.[4] The diamagnetic corrections were also made using Pascal's constants.[5] The thermogravimetric analyses were done on a thermogravimetric analyser model-TGA-FCI-P & D, Sindri, attached with thermocouple model M & M-PCT-5168. The samples were loaded manually in a platinum basket (1 cm x 1 cm) without using any diluent. The samples were analyzed in a temperature range of 20°–900°C, and only the final products were identified.

## RESULTS AND DISCUSSION

All the complexes are insoluble in solvents suitable for molecular weight determination, hence their molecular weight could not be determined. We could not obtain single crystals for X-ray analysis. Therefore, the structures of the complexes have been proposed on the basis of conductance, electronic spectral, magnetic moment, infrared spectral and thermogravimetric studies.

The analytical data show that four molecules of

TABLE I
Analytical data

| Complexes | Color | M.P. (°C) | *% Nitrogen* |  | *% Selenium* |  | *% Co/Ni* |  | *% Hg/Cd/Zn* |  |
|---|---|---|---|---|---|---|---|---|---|---|
|  |  |  | Obs. | Calc. | Obs. | Calc. | Obs. | Calc. | Obs. | Calc. |
| $(py)_4Co(NCSe)_2Hg(SCN)_2(PPh_3)_2$ | pink | 143 | 7.7 | 7.9 | 11.0 | 11.1 | 3.8 | 4.1 | 13.8 | 14.0 |
| $(bipy)_2Co(NCSe)_2Hg(SCN)_2(PPh_3)_2$ | brown | 150(d) | 7.8 | 7.9 | 11.0 | 11.2 | 3.9 | 4.2 | 13.9 | 14.2 |
| $(py)_4Co(NCSe)_2Cd(SCN)_2(PPh_3)_2$ | pink | 210(d) | 8.2 | 8.4 | 11.7 | 11.8 | 4.3 | 4.4 | 8.2 | 8.4 |
| $(bipy)_2Co(NCSe)_2Cd(SCN)_2(PPh_3)_2$ | orange | 220(d) | 8.4 | 8.5 | 11.6 | 11.9 | 4.2 | 4.5 | 8.1 | 8.5 |
| $(py)_4Co(NCSe)_2Zn(SCN)_2(PPh_3)_2$ | pink | 195(d) | 8.5 | 8.7 | 12.0 | 12.2 | 4.5 | 4.6 | 4.9 | 5.0 |
| $(bipy)_2Co(NCSe)_2Zn(SCN)_2(PPh_3)_2$ | orange | 235(d) | 8.8 | 8.8 | 12.3 | 12.4 | 4.4 | 4.6 | 4.9 | 5.1 |
| $(py)_4Ni(NCSe)_2Hg(SCN)_2(PPh_3)_2$ | blue | 170 | 7.6 | 7.9 | 11.0 | 11.1 | 3.9 | 4.1 | 13.8 | 14.0 |
| $(bipy)_2Ni(NCSe)_2Hg(SCN)_2(PPh_3)_2$ | pink | 176(d) | 7.8 | 7.9 | 10.9 | 11.2 | 4.0 | 4.2 | 14.0 | 14.2 |
| $(py)_4Ni(NCSe)_2Cd(SCN)_2(PPh_3)_2$ | blue | 184(d) | 8.2 | 8.4 | 11.7 | 11.8 | 4.3 | 4.4 | 8.3 | 8.4 |
| $(bipy)_2Ni(NCSe)_2Cd(SCN)_2(PPh_3)_2$ | pink | 190(d) | 8.2 | 8.5 | 11.6 | 11.9 | 4.2 | 4.5 | 8.2 | 8.5 |
| $(py)_4Ni(NCSe)_2Zn(SCN)_2(PPh_3)_2$ | pink | 182(d) | 8.6 | 8.7 | 11.9 | 12.2 | 4.5 | 4.6 | 4.8 | 5.0 |
| $(bipy)_2Ni(NCSe)_2Zn(SCN)_2(PPh_3)_2$ | pink | 188(d) | 8.5 | 8.8 | 12.2 | 12.4 | 4.3 | 4.6 | 5.0 | 5.1 |

d = decomposition

pyridine or two molecules of 2,2'bipyridyl and two molecules of triphenylphosphine are coordinated to a molecule of $\rangle \mathrm{M(NCS)(NCSe)M'(SeCN)(SCN)} \langle$. The x-sensitive q, r, t and y (Whiffin's bands) which are the characteristic absorption bands of P–C (aromatic) stretching and bending vibrations of triphenylphosphine are shifted to higher frequencies. These shifts indicate that the ligand is coordinated.[6,7] Similarly in the case of pyridine, the in-plane ring vibrations and the out-of-plane modes are shifted towards higher energies indicating that pyridine is coordinated.[8–10] The changes observed in the infrared spectra of 2,2'bipyridyl indicate that it is coordinated through both of its nitrogen atoms.[11] On the basis of these results a number of structures can be proposed:-

(i) *Cationic-anionic*

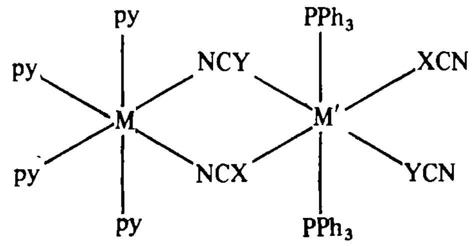
$[\mathrm{M(py)_4(PPh_3)_2}]^{2+}[\mathrm{M'(SCN)_2(SeCN)_2}]^{2-}$ I

(ii) *Polymeric bridged or polynuclear bridged*

$\rangle \mathrm{(py)_4M(NCS)(NCSe)M'(PPh_3)_2(SeCN)(SCN)} \langle$ II

$\rangle \mathrm{(py)_2M(NCS)(NCSe)(Ph_3P)_2M'(py)_2(SCN)(SeCN)} \langle$ III

(iii) *Monomeric bridged or dinuclear bridged*



(*a*. X = S, Y = Se; *b*. Bridged X & Y = S, terminal X & Y = Se; *c*. bridged X & Y = Se, terminal X & Y = S)
*a*. $\mathrm{(py)_4M(NCS)(NCSe)M'(SeCN)(SCN)(PPh_3)_2}$,
*b*. $\mathrm{(py)_4M(NCS)_2M'(SeCN)_2(PPh_3)_2}$, *c*. $\mathrm{(py)_4M(NCSe)_2}$-$\mathrm{M'(SCN)_2(PPh_3)_2}$ IV (a,b,c)

1) The complexes are very sparingly soluble in formamide and their dilute solutions are non-conducting. This rules out the possibility of any cationic–anionic structure.

2) The structures II and III are unlikely, because in these cases either cobalt or mercury becomes eight coordinated, which is untenable. These observations rule out the possibility of polymeric bridged structures.

3) The number of IR bands in the νC–N, νC–S and νC–Se regions in polymeric-bridged complexes are two, one and one, respectively.[1] The observed number of bands in these regions are more, which also indicates that complexes are not polymeric in nature.

4) Structures IV(a, b & c) are the likely structures of the complexes as they satisfy the following requirements:

i) The non conducting nature of the complexes supports a bridged structure.

ii) The positions of infrared bands in the νC–N stretching region indicate the presence of terminal S-bonded, Se-bonded and bridging thio- or selenocyanates. Similarly, the number and positions of bands in the δNCS, δNCSe, νC–S, νC–Se regions also support the presence of both bridging and terminal thio- and selenocyanates. The number and position of these bands support a dinuclear bridged structure.[12–16] The bands in the range 500–775 $\mathrm{cm^{-1}}$ have not been assigned with certainty as ligand bands also appear in this region.[17]

iii) Octahedral coordination geometry of cobalt and nickel as required for the dinuclear bridged structure are supported by the electronic spectral and magnetic moment studies, which are discussed later.

iv) The soft end (S- or Se-) of thiocyanate and selenocyanate is shown linked to M' and the hard end (-N) to M. Similarly the soft triphenylphosphine is shown coordinated to M' and the borderline pyridine to M. These attachments satisfy the HSAB requirements.[18] The quantitative values of softness have been derived by solving the Klopman equation[19] and the results are presented in Table III. The quantitative values also favor linkage of triphenylphosphine to M' and pyridine or bipyridyl to M. The linkage of the N-end to M and X to M' is also supported similarly.[1,19]

v) As presented in Table II, the far infrared region shows the presence of M'–X (X=S, Se), M'–P and M–N stretching modes.[20–23] The presence of these bands also support the proposed structure.

vi) $\rangle \mathrm{M(NCS)(NCSe)M'(SeCN)(SCN)} \langle$ form three type of complexes viz. *cationic–anionic, dinuclear* bridged and polynuclear bridged complexes. Our investigations show that the nature of the curves as presented in Figs. 1 and 2 is identical to the nature of curves of reported dinuclear bridged complexes. This renders an additional support to their proposed structures.

TABLE II
Infrared Spectral Band Assignments of Complexes

| Complexes | NCS pseudo antisym. stretch + NCSe pseudo stretch (C—N stretch) 2A′ + 2A′ | NCS pseudo sym. stretch (C—S stretch) 2A′ | NCSe pseudo sym. stretch (C—Se stretch) 2A′ | M—NCS deformation (NCS) bend) + M—NCSe deformation (NCSe bend) (A′ + A″) + (A′ + A″) | M′—SCN deformation (NCS bend) + M′—SeCN deformation (NCSe bend) (2A′ + 2A″) + (2A′ + 2A″) | Far infrared spectral bands |
|---|---|---|---|---|---|---|
| $(py)_4Co(NCSe)_2Hg(SCN)_2(PPh_3)_2$ | 2140(s), 2120(s)<br>2085 (sh) | 759(s), 750(s)<br>710(s) | 630(s), 570(s)<br>520(s), 500(s) | 430(m), 420(m) | 445(m), 400(s)<br>375(m) | 260(m), 245(s), 218(s)<br>204(s), 170(m), 132(m) |
| $(bipy)_2CoNCSe)_2Hg(SCN)_2(PPh_3)_2$ | 2140(s), 2105(sh)<br>2095(s) | 770(s), 752(s)<br>690(s) | 620(m), 565(s)<br>520(s), 505(s) | 425(m), 410(s) | 440(s), 400(s)<br>385(m) | 276(s), 252(s), 232(m)<br>218(m), 128(s) |
| $(py)_4Co(NCSe_2Cd(SCN)_2(PPh_3)_2$ | 2170(s), 2140(m)<br>2070(sh) | 760(s), 750(s)<br>700(s) | 630(s), 570(s)<br>522(s), 510(s) | 435(s) | 450(s), 405(m)<br>390(m) | 268(s), 242(s), 218(s)<br>203(s), 138(s) |
| $(py)_4Ni(NCSe)_2Hg(SCN)_2(PPh_3)_2$ | 2140(s), 2100(s)<br>2080(s) | 755(s), 750(s)<br>742(s), 690(s) | 652(s), 620(m)<br>570(s), 515(s) | 435(s), 420(m) | 470(s), 455(s)<br>400(m), 380(s) | 318(m), 272(s), 252(s)<br>230(m), 195(s), 122(m) |
| $(bipy)_2Ni(NCSe)_2Hg(SCN)_2(PPh_3)_2$ | 2170(s), 2100(s)<br>2080(s) | 770(s), 760(s)<br>740(s), 690(s) | 655(s), 630(s)<br>565(s), 515(s) | 430(s), 420(s) | 485(m), 455(m)<br>400(s), 380(m) | 322(m), 286(s), 262(s)<br>256(s), 212(m), 138(m) |
| $(bipy)_2Ni(NCSe)_2Cd(SCN)_2(PPh_3)_2$ | 2160(s), 2130(m)<br>2090(sh) | 775(s), 760(s)<br>750(s), 700(s) | 660(s), 570(s)<br>520(s), 515(s) | 432(s), 420(s) | 455(m), 400(s)<br>385(m) | 310(m), 292(s), 266(s)<br>232(m), 221(m), 136(m) |

TABLE III
Quantitative values of softness of metal ions and ligands

| Lewis Base | $E^{\ddagger}_m$ (Softness of ligands) | Lewis Acid (Metal Ions) | $E^{\ddagger}_n$ (Softness of metal ions) |
|---|---|---|---|
| Pyridine | −11.44 | $Co^{2+}$ | −0.22 |
| 2,2′bipyridyl | −11.47 (when it is monodentate)<br>−22.94 (when it is bidentate) | $Ni^{2+}$ | −0.52 |
| | | $Zn^{2+}$ | −1.24 |
| | | $Cd^{2+}$ | −2.26 |
| | | $Hg^{2+}$ | −4.87 |
| Triphenyl-phosphine | −6.78 | | |
| N(—NCSe⁻) | −8.93 | | |
| N(—NCS⁻) | −8.10 | | |
| S(—SCN⁻) | −5.20 | | |
| Se(—SeCN⁻) | −4.41 | | |

Each complex finally decomposes to $Co_3O_4$ or NiO along with CdO or ZnO through the formation of an intermediate. In thermogravimetric analysis of all these complexes we get two breaks in each case.

a) The first break is due to the elimination of ligands and it depends upon the nature of Lewis bases. If ligand is 2,2′-bipyridyl or triphenylphosphine, only one smooth break is observed which shows that these ligands are removed continuously. In case of pyridine two breaks are observed instead of one. This shows that out of four pyridine molecules only two are removed at a time.

b) The second break is due to the elimination of thiocyanates and selenocyanates. The thiocyanates are removed earlier than the selenocyanates.

vii) Assuming $C_s$ point group symmetry for the structure IV(a) and $C_{2v}$ point-group symmetry for the structures IV(b and c), the number of normal modes for $\nu$C—N, $\nu$C—S, $\nu$C—Se and $\delta$NCS, $\delta$NCSe have been calculated. Unfortunately the number of calculated bands for these two point groups in the region $\nu$C—N, $\nu$C—S, $\nu$C—Se, $\delta$NCS, $\delta$NCSe are the same. Hence structures IV(a, b, and c) could not be differentiated. However, these calculations support these three structures. It is worth noting that structures IV(a, b and c) are the geometrical isomers, hence it can be concluded that the complexes are either a mixture or one of these three isomers.

*Electronic Spectral Discussion*

To confirm the proposed coordination geometry of cobalt and nickel we have recorded the electronic spectra as Nujol mull and magnetic moment values

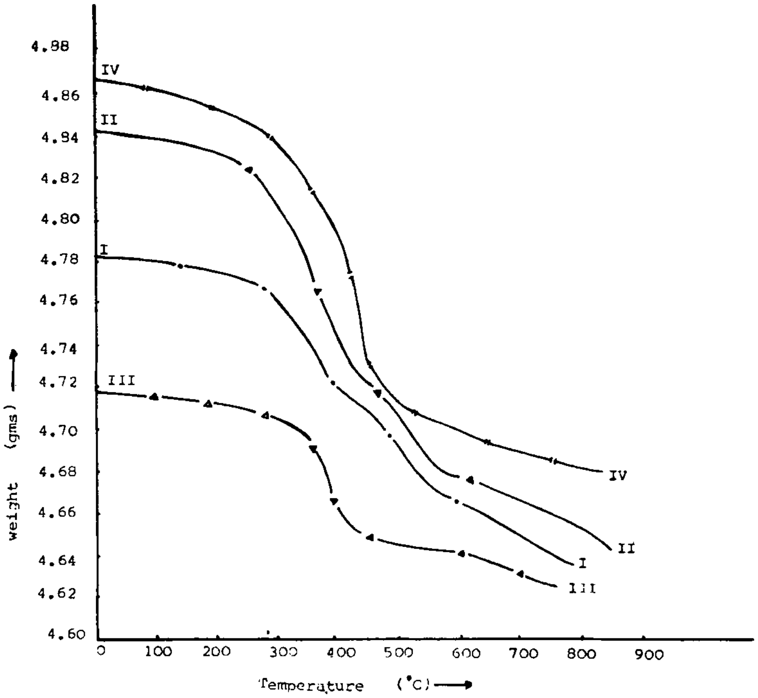


FIGURE 1 Thermogravimetric curves of complexes[1]. I. $(bipy)_2Co(NCSe)_2Hg(SCN)_2$; II. $(bipy)_2Ni(NCSe)_2$-$Hg(SCN)_2$; III. $(Ph_3P)_2Co(NCSe)_2Hg(SCN)_2$; IV. $(Ph_3P)_2Ni(NCSe)_2Hg(SCN)_2$.

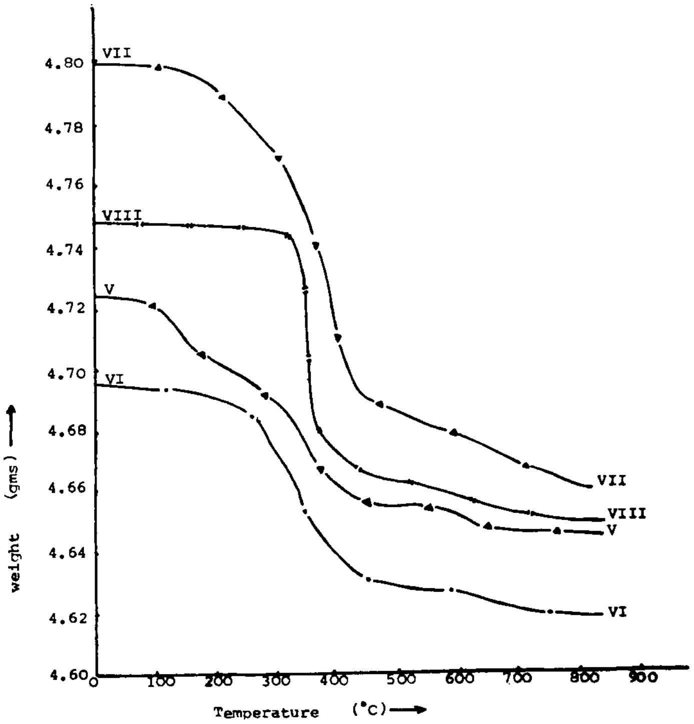


FIGURE 2 Thermogravimetric curves of complexes[2,7] V. $(py)_4Co(NCSe)_2Hg(SCN)_2(PPh_3)_3$; VI. $(bipy)_2$-$Co(NCSe)_2Hg(SCN)_2(PPh_3)_2$; VII. $(py)_4Ni(NCSe)_2Hg(SCN)_2(PPh_3)_2$; VIII. $(bipy)_2Ni(NCSe)_2Hg(SCN)_2(PPh_3)_2$.

TABLE IV

Electronic Spectral Band Position and their Assignments in cm$^{-1}$. Spectral Parameters and Magnetic Moment Values

| Complexes | $^3T_{1g}(P) \leftarrow {}^3A_{2g}$ $(\nu_3)$ | $^3T_{1g}(F) \leftarrow {}^3A_{2g}$ $(\nu_2)$ | $^3T_{2g}(F) \leftarrow {}^3A_{2g}$ $(\nu_1)$ | Dq | B′ | β | $\mu_{eff}$ |
|---|---|---|---|---|---|---|---|
| $(py)_4Ni(NCSe)_2Hg(SCN)_2(PPh_3)_2$ | 29,800 | 17,700 | 10,400 | 1,079 | 1,009 | 0.97 | 3.06 |
| $(py)_4Ni(NCSe)_2Cd(SCN)_2(PPh_3)_2$ | 29,100 | 17,000 | 10,200 | 1,037 | 999 | 0.96 | 3.09 |
| $(bipy)_2Ni(NCSe)_2Zn(SCN)_2(PPh_3)_2$ | 28,600 | 17,000 | 10,300 | 1,043 | 954 | 0.92 | 3.12 |
| | $^4T_{1g}(P) \leftarrow {}^4T_{1g}(F)$ | $^4A_{2g} \leftarrow {}^4T_{1g}(F)$ | $^4T_{2g}(F) \leftarrow {}^4T_{1g}(P)$ | | | | |
| $(py)_4Co(NCSe)_2Hg(SCN)_2(PPh_3)_2$ | 21,300 | 13,800 | 9,200 | | | | 5.08 |
| $(bipy)_2Co(NCSe)_2Cd(SCN)_2(PPh_3)_2$ | 20,900 | 18,500 | 9,600 | | | | 5.02 |
| $(bipy)_2Co(NCSe)_2Zn(SCN)_2(PPh_3)_2$ | 21,200 | 18,800 | 9,800 | | | | 5.06 |

of all the complexes, the results of which are included in Table IV.

In the case of the cobalt complexes three bands are observed in the regions 9100–9800 cm$^{-1}$, 17800–18800 cm$^{-1}$ and 20900–22000 cm$^{-1}$, which are assigned to the transitions $^4T_{2g} \leftarrow {}^4T_{1g}(\nu_1)$, $^4A_{2g} \leftarrow {}^4T_{1g}(\nu_2)$ and $^4T_{1g}(P) \leftarrow {}^4T_{1g}(\nu_3)$. The $\nu_1$ is generally broad and $\nu_3$ is a multiple band and may be mixed with spin forbidden transition. The $\nu_2$ band is very weak. The positions and nature of these bands indicate that cobalt in these complexes is in an octahedral coordination geometry. Magnetic moment values also support this geometry.

In all nickel complexes, three bands are observed in the regions 9900–10700 cm$^{-1}$, 16800–17700 cm$^{-1}$ and 28600–29800 cm$^{-1}$ which are assigned to the transitions $^3T_{2g} \leftarrow {}^3A_{2g}(\nu_1)$, $^3T_{1g} \leftarrow {}^3A_{2g}$ $(\nu_2)$ and $^3T_{1g}(P) \leftarrow {}^3A_{2g}(\nu_3)$.

We have calculated Dq, B′ and β values of nickel(II) complexes with the help of matrices of Tanabe and Sugano,[24] using the values of $\nu_2$ and $\nu_3$. The electronic spectral band positions, spectral parameters and magnetic moment values very clearly indicate that nickel in all these complexes has octahedral coordination geometry.[25] The Dq values are in the range reported[15] for $[(py)_4Ni(NCSe)_2]$ and $[(bipy)_2Ni(NCSe)_2]$. Had triphenylphosphine been linked to nickel, the difference in Dq values would have been more.

### $\Delta TE_n^{\ddagger}(M{-}M')$ *and the complexes*

The stabilities of thiocyanate and selenocyanate bridges in $\rangle M(NCSe)_2M'(SeCN)_2\langle$, $\rangle M(NCS)_2M'(SCN)_2\langle$ and $\rangle M(NCS)(NCSe)M'(SeCN)(SCN)\langle$ have been related to the difference in total softness values $[\Delta TE_n^{\ddagger}(M{-}M')]^1$ of M and M′. It has been shown that the higher values of $\Delta TE_n^{\ddagger}(M{-}M')$ the greater is the stability of the bridge. We have now calculated the total softness values of M and M′ in $(PPh_3)_2Co(NCSe)_2Hg(SCN)_2$ and $(SCN)_2Co(NCSe)_2Hg(PPh_3)_2$, by adopting the following equations:

*For* $(PPh_3)_2Co(NCSe)_2Hg(SCN)_2$

$$TE_n^{\ddagger}(Co) = E_n^{\ddagger}(Co) + 2E_m^{\ddagger}(NCSe) + 2E_m^{\ddagger}(PPh_3)$$

$$TE_n^{\ddagger}(Hg) = E_n^{\ddagger}(Hg) + 2E_m^{\ddagger}(SCN) + 2E_m^{\ddagger}(SeCN)$$

$$\Delta TE_n^{\ddagger}(Co{-}Hg) = TE_n^{\ddagger}(Hg) - TE_n^{\ddagger}(Co)$$

*For $(SCN)_2Co(NCSe)_2Hg(PPh_3)_2$*

$$TE_n^\ddagger(Co) = E_n^\ddagger(Co) + 2E_m^\ddagger(NCS) + 2E_m^\ddagger(NCSe)$$

$$TE_n^\ddagger(Hg) = E_n^\ddagger(Hg) + 2E_m^\ddagger(SeCN) + 2E_m^\ddagger(PPh_3)$$

$$\Delta TE_n^\ddagger(Co{-}Hg) = TE_n^\ddagger(Hg) - TE_n^\ddagger(Co)$$

The $\Delta TE_n^\ddagger(M{-}M')$ values in case of $(PPh_3)_2Co(NCSe)_2Hg(SCN)_2$ comes to 7.55 and in case of $(SCN)_2Co(NCSe)_2Hg(PPh_3)_2$ to 7.03. Since, the value of $\Delta TE_n^\ddagger(M{-}M')$ is higher in case of $(PPh_3)_2Co(NCSe)_2Hg(SCN)_2$, it can be presumed that this is the possible reason for the attachment of triphenylphosphine on cobalt instead of mercury as shown earlier.[1,2 6]

The $\Delta TE_n^\ddagger(M{-}M')$ values in respect of structures IV(a, b and c) have also been derived similarly, and the results are presented in Table V.

The $\Delta TE_n^\ddagger(M{-}M')$ values for structure IV(c) is higher for every complex, as compared to the values derived for alternative structures IV(a) and IV(b). Since the value of $\Delta TE_n^\ddagger(M{-}M'$ is highest in case of structure IV(c), it can be presumed that this is the most plausible structure of the complexes.

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TABLE V
Total softness values of M and M′, and their differences in complexes

| Complexes | $TE_n^\ddagger(M)$ | $TE_n^\ddagger(M')$ | $\Delta TE_n^\ddagger(M{-}M')$ |
|---|---|---|---|
| $(py)_4Co(NCS)(NCSe)Hg(SeCN)(SCN)(PPh_3)_2$ | −63.01 | −37.65 | 25.36 |
| $(py)_4Co(NCS)_2Hg(SeCN)_2(PPh_3)_2$ | −62.18 | −37.65 | 24.53 |
| $(py)_4Co(NCSe)_2Hg(SCN)_2(PPh_3)_2$ | −63.84 | −37.65 | 26.19 |
| $(bipy)_2Co(NCS)(NCSe)Hg(SeCN)(SCN)(PPh_3)_2$ | −63.13 | −37.65 | 25.48 |
| $(bipy)_2Co(NCS)_2Hg(SeCN)_2(PPh_3)_2$ | −62.30 | −37.65 | 24.65 |
| $(bipy)_2Co(NCSe)_2Hg(SCN)_2(PPh_3)_2$ | −63.96 | −37.65 | 26.31 |
| $(py)_4Co(NCS)(NCSe)Cd(SeCN)(SCN)(PPh_3)_2$ | −63.01 | −35.04 | 27.97 |
| $(py)_4Co(NCS)_2Cd(SeCN)_2(PPh_3)_2$ | −62.18 | −35.04 | 27.14 |
| $(py)_4Co(NCSe)_2Cd(SCN)_2(PPh_3)_2$ | −63.84 | −35.04 | 28.80 |
| $(bipy)_2Co(NCS)(NCSe)Cd(SeCN)(SCN)(PPh_3)_2$ | −63.13 | −35.04 | 28.09 |
| $(bipy)_2Co(NCS)_2Cd(SeCN)_2(PPh_3)_2$ | −62.30 | −35.04 | 27.26 |
| $(bipy)_2Co(NCSe)_2Cd(SCN)_2(PPh_3)_2$ | −63.96 | −35.04 | 28.92 |
| $(py)_4Co(NCS)(NCSe)Zn(SeCN)(SCN)(PPh_3)_2$ | −63.01 | −34.02 | 28.99 |
| $(py)_4Co(NCS)_2Zn(SeCN)_2(PPh_3)_2$ | −62.18 | −34.02 | 28.16 |
| $(py)_4Co(NCSe)_2Zn(SCN)_2(PPh_3)_2$ | −63.84 | −34.02 | 29.82 |
| $(bipy)_2Co(NCS)(NCSe)Zn(SeCN)(SCN)(PPh_3)_2$ | −63.13 | −34.02 | 29.11 |
| $(bipy)_2Co(NCS)_2Zn(SeCN)_2(PPh_3)_2$ | −62.30 | −34.02 | 28.28 |
| $(bipy)_2Co(NCSe)_2Zn(SCN)_2(PPh_3)_2$ | −63.96 | −34.02 | 29.94 |
| $(py)_4Ni(NCS)(NCSe)Hg(SeCN)(SCN)(PPh_3)_2$ | −63.31 | −37.65 | 25.66 |
| $(py)_4Ni(NCS)_2Hg(SeCN)_2(PPh_3)_2$ | −62.48 | −37.65 | 24.83 |
| $(py)_4Ni(NCSe)_2Hg(SCN)_2(PPh_3)_2$ | −64.14 | −37.65 | 26.49 |
| $(bipy)_2Ni(NCS)(NCSe)Hg(SeCN)(SCN)(PPh_3)_2$ | −63.43 | −37.65 | 25.78 |
| $(bipy)_2Ni(NCS)_2Hg(SeCN)_2(PPh_3)_2$ | −62.60 | −37.65 | 24.95 |
| $(bipy)_2Ni(NCSe)_2Hg(SCN)_2(PPh_3)_2$ | −64.26 | −37.65 | 26.61 |
| $(py)_4Ni(NCS)(NCSe)Cd(SeCN)(SCN)(PPh_3)_2$ | −63.31 | −35.04 | 28.27 |
| $(py)_4Ni(NCS)_2Cd(SeCN)_2(PPh_3)_2$ | −62.48 | −35.04 | 27.44 |
| $(py)_4Ni(NCSe)_2Cd(SCN)_2(PPh_3)_2$ | −64.14 | −35.04 | 29.10 |
| $(bipy)_2Ni(NCS)(NCSe)Cd(SeCN)(SCN)(PPh_3)_2$ | −63.43 | −35.04 | 28.39 |
| $(bipy)_2Ni(NCS)_2Cd(SeCN)_2(PPh_3)_2$ | −62.60 | −35.04 | 27.56 |
| $(bipy)_2Ni(NCSe)_2Cd(SCN)_2(PPh_3)_2$ | −64.26 | −35.04 | 29.22 |
| $(py)_4Ni(NCS)(NCSe)Zn(SeCN)(SCN)(PPh_3)_2$ | −63.31 | −34.02 | 29.29 |
| $(py)_4Ni(NCS)_2Zn(SeCN)_2(PPh_3)_2$ | −62.48 | −34.02 | 28.46 |
| $(py)_4Ni(NCSe)_2Zn(SCN)_2(PPh_3)_2$ | −64.14 | −34.02 | 30.12 |
| $(bipy)_2Ni(NCS)(NCSe)Zn(SeCN)(SCN)(PPh_3)_2$ | −63.43 | −34.02 | 29.41 |
| $(bipy)_2Ni(NCS)_2Zn(SeCN)_2(PPh_3)_2$ | −62.60 | −34.02 | 28.58 |
| $(bipy)_2Ni(NCSe)_2Zn(SCN)_2(PPh_3)_2$ | −64.26 | −34.02 | 30.24 |

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