Quantitative Values of Softness & Structure of Bimetallic Tetra- thiocyanate, Tetraselenocyanate & Dithiodiselenocyanate Complexes

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Bimetallic tetrathiocyanates, tetraselenocyanates and mixed dithiodiselenocyanates of the type MHg (SCN)₄, xL, MHg (SeCN)₄, xL and MHg (SCN)₂ (SeCN)₂, xL [M=Co(II); Ni(II); L=ethylenurea, ethylenedithiourea, N, N-dimethyl-urea, N, N-dimethylthiourea, thiazolidine-2-thione; x=2, 4] have been synthesized. Their structures have been proposed on the basis of infrared and electronic spectral, magnetic moment and molar conductance studies. The structures proposed are supported by quantitative softness values of metal ions and ligands. The relative strengths of thiocyanate and selenocyanate bridges have been correlated with the total softness difference $\Delta T_{E_{T}}^{(M-M')}$. A new series of complexes of >M(NCS)₂Hg-(SCN)₂<, >M(NCS)₂Hg(SeCN)₂< and >M(NCS)(NCSe)Hg(SeCN)(SCN)< [M = Co(II), Ni(II)] have been synthesized. Their structures were prepared as described elsewhere.

Materials and Methods

All the chemicals used were of AR grade. Potassium selenocyanate was prepared as described elsewhere. Preparation of the complexes — Lewis-acids, viz. >M(NCS)₂Hg(SeCN)₂<, >M(NCS)₂Hg(SeCN)₂< and >M(NCS)(NCSe)Hg(SeCN)(SCN)< [M = Co(II), Ni(II)] were prepared by the methods described earlier. Their complexes were prepared by stirring the Lewis acid and the ligand (1:2 molar ratio for cobalt complexes and 1:4 molar ratio for nickel complexes) in 50 ml ethanol for 48 hr. The ligand was always kept in a slight excess. The reaction mixture was filtered and the complex obtained was washed with the solvent and dried in vacuo.

The complexes were analysed for sulphur as barium sulphate, selenium as selenium metal, nickel as dimethylglyoximate, mercury as sulphide and cobalt as anthranilate gravimetrically. Nitrogen was estimated by Kjeldahl's method. The results are recorded in Table 1 along with m.p. and colour data.

The infrared spectra of the complexes were recorded in the range 4000-200 cm⁻¹ on a Perkin-Elmer spectrophotometer model 621. The electronic spectra were recorded in the range 1800-300 nm in nujol by adopting the procedure employed by Lee on a Carl Zeiss spectrophotometer model DMR 21. Magnetic susceptibility measurements were made at room temperature by Gouy's method using Co[Hg(SCN)₄] as the standard. The diamagnetic corrections were made according to Figgis. Molar conductances were measured in DMF using a Philips PR-9500 conductivity bridge.

Results and Discussion

The complexes have been divided into two groups (i) monomeric bridged and (ii) polymeric bridged complexes.

(i) The molar conductance values (Table 1) of these complexes in DMF are in the range 19.8-24.3 ohm⁻¹ cm² mole⁻¹ indicating that they are non-electrolytes.

(ii) The electronic spectra, colour and magnetic moment values of these complexes as discussed later show that cobalt and nickel are present in tetrahedral and octahedral environments respectively.

(iii) The IR spectra show the presence of two to three bands in C≡N region (2150-2080 cm⁻¹), which shows the presence of both terminal and bridged thiocyanate or selenocyanate groups. The bands around 2150 and 2080 cm⁻¹ are assigned to the bridged and terminal S-bonded thiocyanates respectively. This is also supported by the positions and number of bands assigned to δ NCS, δ NCSe, ν C=—S and ν CSe modes. The bands in the range 510-770 cm⁻¹ have not been assigned with certainty as some of the ligand bands also appear in this region.
(v) The softness values of imino nitrogen in thiazolidine-2-thione (tzt), ethylenethiourea (etu), and N,N'-dimethylthiourea (dmtu) and carbonyl oxygen in ethyleneurea (eu) and dmtu, as calculated from Klopman’s equation\(^9\) show more compatibility with cobalt and nickel as compared to mercury. Therefore, the ligands are coordinated to cobalt or nickel.

(vi) Comparison of the calculated \(Dq\) values of these complexes with reported \(Dq\) values\(^{10,11}\) of the similar complexes indicates that cobalt is surrounded by two ligands and two thio or selenocyanate groups while nickel is surrounded by four ligands and two thio or selenocyanate groups.

On the basis of the above results the following (I-VI) are the most plausible structures of these monomeric bridged complexes.

For nickel(II) complexes the proposed structures are similar except that the number of ligands (L) is four. The above structures pose one main problem i.e. whether the ligands are attached to cobalt or to mercury (I & II, III & IV, V & VI). It is difficult to establish the correct structures, with the help of infrared and electronic spectral studies, however, quantitative softness values as discussed later support the structure I, III and V.

Donor sites in the ligands — The ligands have two or three potential donor sites. The actual positions of coordination have been distinguished.
with the help of IR spectra of the complexes and the ligands.

$v(C=O)$ frequency in the IR spectra of complexes of eu shows a negative shift of 98-118 from its position in the ligand (1718) indicating coordination of eu through the carbonyl oxygen. In the IR spectra of dmu the band positions of $v(N-H)$, $\delta(NH)$ and $v(C=O)$ were assigned at 3325, 1560 and 1642 respectively. On comparing these values with those of its complexes it is found that there is a negative shift of 42 in $v(C=O)$, a positive shift of 95 in $v(N-H)$ and a negative shift in $\delta(N-H)$. This shows that dmu is coordinated through carbonyl oxygen and not through nitrogen of its imino group.

In etu complexes it is observed that there is a negative shift of 75-185 in $v(N-H)$ indicating coordination through nitrogen. The assignment of the thiocarbonyl band is not definite. However, the most accepted assignment of the bands indicating the presence of two intense bands in the range 1600-1700 and 7000-8000 cm$^{-1}$ which are assigned to the transitions $4T_{1g} (p) \rightarrow 4A_{2g} (v_3)$ and $4T_{1g} (F) \rightarrow 4A_{2g} (v_2)$ respectively. With the help of the positions of $v_2$ and $v_3$ bands, we have derived the spectral parameters $D_q$, $B'$ and $\beta$. The band positions and the values of spectral parameters clearly indicate that the cobalt is in tetrahedral environment. The $v_3$ absorption splits into 2-3 bands indicating the presence of $C_{2v}$ symmetry around cobalt. The $D_q$ values of these complexes with the help of IR spectra of the complexes and the ligands.

Various X-ray studies have indicated sulphur as the donor site in etu. Some workers have however shown that imino nitrogen is the donor site in this ligand. It can therefore be conceived that the site of coordination changes according to the environment around the metal ion. The coordination site in etu and dmtu in the present case is imino nitrogen, and such a linkage may be due to the presence of NCSe groups around Co(II) or Hg(II).

**Polymetric bridged complexes, viz. $>(SeCN)_{2}Ni(NCS)(NCSe)Hg<$ and $>(SeCN)_{2}Ni(NCS)(NCSe)_{2}Hg<$(L = dmu, dmtu, eu, etu, tzt)** — These complexes are characterized as polymetric bridged type on account of their following differences from monomeric bridged complexes.

(i) Analytical results show that only two ligands are coordinated to each molecule of the lewis acid, hence the octahedral coordination geometry for nickel can be achieved only through polymetric bridged structure.

(ii) The electronic spectra in solid phase, colur and magnetic moment values clearly show that in these complexes nickel is in octahedral geometry.

(iii) The IR spectra show the presence of one or two bands in $vC \equiv N$ region above 2120 and absence of bands below 2120. The positions of the bands due to $vC=Se$ and $\delta NCSe$ are in the range 570-550 and 390-140 respectively. The positions of these bands indicate that the selenocyanate groups are in the bridged state. In mixed dithio and diselenocyanate complexes the positions of $vC-X$ and $\delta NCX (X = S, Se)$ reveal that they are also in bridged state.

On the basis of the above and earlier observations the following structures can be proposed.

The electronic spectra of cobalt complexes show the presence of two intense bands in the range 16000-17000 and 7000-8000 cm$^{-1}$ which are assigned to the transitions $4T_{1g} (p) \rightarrow 4A_{2g} (v_3)$ and $4T_{1g} (F) \rightarrow 4A_{2g} (v_2)$ respectively. With the help of the positions of $v_2$ and $v_3$ bands, we have derived the spectral parameters $D_q$, $B'$ and $\beta$. The band positions and the values of spectral parameters clearly indicate that the cobalt is in tetrahedral environment. The $v_3$ absorption splits into 2-3 bands indicating the presence of $C_{2v}$ symmetry around cobalt. The $D_q$ values of these complexes
Table 2: Calculated Differences of Total Softness Values, $\Delta TE^+_n$ (M-M')

<table>
<thead>
<tr>
<th>Lewis Acids</th>
<th>$\Delta TE^+_n$ (M-M') of ligands</th>
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<tr>
<td></td>
<td>tzt N-bonded S-bonded</td>
</tr>
<tr>
<td>$\text{Co(NCS)}_2 \text{Hg(SCN)}_2$</td>
<td>14.01 6.37</td>
</tr>
<tr>
<td>$\text{Co(NCS)}_2 \text{Hg(SCN)}_2$</td>
<td>16.42 8.78</td>
</tr>
<tr>
<td>$\text{Co(NCS)}_2 \text{Hg(SCN)}_2$</td>
<td>18.83 11.19</td>
</tr>
<tr>
<td>$\text{Ni(NCS)}_2 \text{Hg(SCN)}_2$</td>
<td>37.58 22.30</td>
</tr>
<tr>
<td>$\text{Ni(NCS)}_2 \text{Hg(SCN)}_2$</td>
<td>33.76 26.12</td>
</tr>
<tr>
<td>$\text{Ni(NCS)}_2 \text{Hg(SCN)}_2$</td>
<td>37.00 29.36</td>
</tr>
</tbody>
</table>

Softness values of ligands

are in the range 420-475 cm$^{-1}$, which is very close to the $Dq$ values of Co(NCS)$_2$. The closeness in $Dq$ values and the split nature of $\nu_2$ band also support the proposed structure.

In nickel complexes, bands are observed in the region 16,100-17000 and 26,600-28,100 cm$^{-1}$ which are assigned to the transitions $^3T_{1u} (F) \rightarrow ^3T_{2g}$ and $^3T_{1g} (P) \rightarrow ^5A_{2g}$ ($\nu_3$) respectively. Spectral parameters $Dq$, $B'$ and $\beta$ have been derived by using the values of $\nu_2$ and $\nu_3$. The positions of bands and the values of these parameters, clearly show that nickel is in octahedral geometry.

$\Delta TE^+_n$ (M-M') and the complexes — The stability of thiocyanate and selenocyanate bridges in M(NCS)$_2$, M'(SCN)$_2$, M(NCSe)$_2$, M'(SeCN)$_2$ and M(NCSe)(SeCN) have been correlated with the difference in total softness values, $\Delta TE^+_n$ (M-M'), of M and M'. It has been shown that a higher value of $\Delta TE^+_n$ (M-M') indicates greater stability of the bridge. We have calculated the total softness values of M and M' in various complexes by adopting standard equations.

The site which gives higher $\Delta TE^+_n$ (M-Hg) value in the present complexes is the possible donor site.

The $\Delta TE^+_n$ (M-Hg) values suggest (Table 2) that imino nitrogens in etu, dmtu and tzt are the donor sites in the complexes. The symbiosis theory also supports coordination through imino nitrogen of the ligand in such a case.

(ii) In the case of monomeric bridged complexes, it is difficult to distinguish between the two structures I and II on the basis of infrared or electronic spectral studies. The $\Delta TE^+_n$ (M-M') values can however resolve this difficulty. The $\Delta TE^+_n$ (Co-Hg) values in respect of structure I and II (L = tzt) are 14.01 and 6.37 respectively indicating that I is the probable structure. The quantitative softness values of the ligands are also more close to the quantitative values of cobalt as compared to those of mercury. Hence, on the basis of HSAB principle, coordination of ligands to cobalt is more probable.

(iii) With the help of total softness values the relative strength of thiocyanate or selenocyanate bridge can be established. The $\Delta TE^+_n$ (M-M') values derived for CoHg (SCN)$_2$, CoHg(SeCN)$_2$/SCN), CoHg (SeCN)$_2$ and NiHg(SCN)$_2$, NiHg(SeCN)$_2$/SCN) suggest the following order of the bridge stability: Co(NCSe)$_2$Hg(SeCN)$_2$ > Co(NCSe)(SeCN)Hg(SCN)$_2$ > Co(NCSe)(SeCN)Hg(SeCN)$_2$ > Ni(Hg)(SCN)$_2$.$\text{Ni}(\text{SCN})_2$.NiHg(SeCN)$_2$. NiHg(SeCN)$_2$ suggest the following order of the bridge stability: Co(NCSe)$_2$Hg(SeCN)$_2$ > Co(NCSe)(SeCN)Hg(SCN)$_2$ > Co(NCSe)(SeCN)Hg(SeCN)$_2$ > Ni(Hg)(SCN)$_2$.$\text{Ni}(\text{SCN})_2$.NiHg(SeCN)$_2$. NiHg(SeCN)$_2$ suggest the following order of the bridge stability: Co(NCSe)$_2$Hg(SeCN)$_2$ > Co(NCSe)(SeCN)Hg(SCN)$_2$ > Co(NCSe)(SeCN)Hg(SeCN)$_2$ > Ni(Hg)(SCN)$_2$.$\text{Ni}(\text{SCN})_2$.NiHg(SeCN)$_2$.

(iv) The $\Delta TE^+_n$ (Co-Hg) values for the monomeric bridged complexes of cobalt in which cobalt is in tetrahedral coordination geometry have been calculated for all the reported complexes. This value in such complexes lies in the range 12.33-18.83. In the case of monomeric bridged nickel complexes this range is 32.08-37.59.

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References