CHAPTER 12

SPECTROSCOPIC STUDY OF TERNARY CT COMPLEXES BASED ON THE ORGANOMETALLIC DONOR-BIS (DIPHENYL-GLYOXIMATO) Ni^{II}
12.1 INTRODUCTION:
There have been a large number of research studies on purely organic binary charge transfer (CT) complexes [1-3]. However, the binary CT complexes involving organometallic chelate as an electron-donor or an electron-acceptor have been limited [4,5]. Some studies of electrical resistivity measurements and infrared transmission spectroscopy were reported for the CT complexes of such metal-organic systems [6-16]. These studies included spectroscopy of binary CT complexes of bis (dimethylglyoximato) Ni^II and bis (diphenylglyoximato) Ni^II. The CT complexes of metal chelates showed indirect transition across the band gap lying in the IR range as compared to direct transition in purely organic CT complexes across a similar gap [17-19]. The indirect transition was attributed to the metal-ligand vibrations in a chelate interacting with electronic motions. This was also verified for phthalocyanine ligand [20,21]. Some of the binary complexes based on bis (N-R-salicylaldiminato)M^II have shown semi-metallic nature with negative band gap [22]. Here we report study of the ternary CT complexes based on Ni(Hdpg)₂ which are found to have semi-metallic nature on the bases of their spectroscopic study.

12.2 EXPERIMENTAL:
The three binary complexes namely Ni(Hdpg)₂ -I₂ Ni(Hdpg)₂-TCNE and Ni(Hdpg)₂ -chloranil where TCNE = N,N,N',N'-tetracyano ethylene were prepared by grinding red-coloured Ni(Hdpg)₂ with iodine, chloranil and TCNE as acceptors in 1:1 molecular weight proportions.

The four ternary complexes namely Ni(Hdpg)₂-TCNQ-I₂, Ni(Hdpg)₂-TCNE-I₂, Ni(Hdpg)₂-Chloranil-I₂ and Ni(Hdpg)₂-DDQ-I₂ were prepared were TCNQ = 7,7,8,8-tetracyano-1,4-quinodimethane and DDQ = 2,3- dichloro -5,6-dicyano-p-benzoquinone. The preparation included of one donor and two acceptors (one being iodine) in equal molecular weight proportion in an eggate mortar with a paste for half-an-hour.

The infrared spectra were recorded in the full range 400-4000 cm⁻¹ using a standard Perkin-Elmer spectrophotometer. The samples used for these measurements were in the form of KBr-based semitransparent pellets using 95% spectrograde KBr powder which was moisture-free and 5% of the binary and ternary complexes.
12.3 RESULTS AND DISCUSSION:

The molecular structures of Ni(Hdpg)$_2$ and organic acceptors used in the present study are shown [Figure 12.1]. The infrared spectra of Ni(Hdpg)$_2$ – the methyl analog and Ni(Hdpg)$_2$ are shown for comparison [Figure 12.2]. The full spectrum is divided in four parts as marked. The first part between 4000 cm$^{-1}$ and 2400 cm$^{-1}$ contain certain stretching vibrations. A band due to intramolecular hydrogen bonding O-H---O bond is seen around 3000 cm$^{-1}$ and is broad due to statistical spread in molecular packing. The region between 2400 cm$^{-1}$ and 1700 cm$^{-1}$ contains constant transmission or absorption. The full spectrum of Ni(Hdpg)$_2$ [Figure 12.3] also contain above two regions but the band due to hydrogen bond around 3300 cm$^{-1}$ is very much intense because of absence of molecular orientations by 90° found in Ni(Hdmg)$_2$ due to interlocking structure. The other change in the second region is drop in transmission (increase in absorption) as wave number decreases. This is similar to the binary complexes of bis(N-R-salicylidininato)Ni$^{ll}$ where R=H, CH$_3$, C$_2$H$_5$ and C$_6$H$_5$ with some acceptors in which a negative activation energies are found. The third part between 1700 cm$^{-1}$ and 1000 cm$^{-1}$ contains a broad background Gaussian band in Ni(Hdpg)$_2$ which is related with Gaussian spread of Ni-Ni distances verified with electrical resistivities at high pressures [5]. The spectrum of Ni(Hdpg)$_2$ also contains such a Gaussian but broader and asymmetric with high energy tail. This Gaussian band is centered around 3500 cm$^{-1}$ (Figure 2b). There is one more very broad and somewhat intense Gaussian band in background absorption around 800 cm$^{-1}$. The presence of two Gaussian bands in Ni(Hdpg)$_2$ reveals presence of two periodicities along the nickel chains. The fourth lowest frequency region between 1000 cm$^{-1}$ and 400 cm$^{-1}$ contains one or two rocking and wagging modes in both of the dioximes but differs in an intense Gaussian-shaped background absorption band in Ni(Hdpg)$_2$ [Figure 12.3].
Figure 12.1 Molecular structures of two metal dioximes and organic acceptors.
Figure 12.2 Infrared spectra of (a) Ni(Hdmg)$_2$ and (b) Ni(Hdpg)$_2$. 
Figure 12.3 (a) IR spectrum of Ni(Hdpg)$_2$; (b) one of the Gaussian bands fitted from the spectrum; (c) direct transition observed in the IR range; and (d) verification of Acoustic phonon scattering.

The comparison between the spectra of Ni(Hdmg)$_2$ and Ni(Hdpg)$_2$ indicates a reduction in the phenyl dioximate increasing the nickel-nickel distance to 3.52 Å which is 3.25 Å in the methyl dioxime chelate. The two Gaussian bands in Ni(Hdpg)$_2$ spectrum reveal two periodicities as found in oligoanilines and their iodine.
complexes [23]. The fully oxidized pernigraniline should be compared with oxidized nickel chain dioximes studied earlier [6]. The Gaussian band related with lesser nickel-nickel distance is retained in the spectrum of Ni(Hdpg)$_2$ because of ligand similarity except the substituted methyl or phenyl group. In Ni(Hdpg)$_2$, there is stacking of phenyl rings parallel to metal chains. The repulsive interactions of bulky phenyl groups and among the $\pi$-clouds increases the intermolecular distance in Ni(Hdpg)$_2$ but nickel ion is chemically reduced leaving scope for oxidation by highly electronegative electron acceptors. Thus Ni(Hdpg)$_2$ is better than Ni(Hdmg)$_2$ in forming highly conducting complexes.

The Gaussian distribution described by

$$A = A_0 \exp \left( -\frac{(K - K_0)^2}{2M_2} \right)$$

where $A$ is absorbance, $K_0$ is the central wavenumber and $M_2$ is the second moment of the distribution, is fitted by plotting $\ln A$ vs $(K - K_0)^2$. This fit for the low-energy Gaussian band in the spectrum of Ni(Hdpg)$_2$ is shown [Figure 12.3b]. The widths of the Gaussian bands are determined by electron-phonon interactions. However, the maximum absorption $(\alpha_{\text{max}})$ depends on the concentration of free charge carriers.

The absorption envelopes can also be fitted as either maximum absorption profile or by joining the inflexion points of the dispersion and absorption profiles instead of plotting the background profiles. All the three kinds of continuous envelopes are plotted [Figure 12.2b].

Other important analysis is regarding the nature of transition which is found as a direct allowed transition in Ni(Hdpg)$_2$ given by

$$\alpha h\nu = A(h\nu - E_g)^{1/2}$$

with $E_g = 0.46\text{eV}$. This band gap is different from the band gap along the metal chains which lies in uv-visible range. The low band gap reveals the overlapping of
phenyl orbitals perpendicular to the metal chains and is related with molecular polarizability of molecules. This absorption function is fitted [Figure 12. 3c].

The final analysis of free-carrier absorption is carried out to plot \( \log \alpha \text{ vs } \log \lambda \) and the slope reveals scattering of electrons by acoustic phonons in the range \( h\nu > E_g = 0.2 \text{ eV} \). This shows that the conduction band is stabilized in the direction transverse to metal chains [Figure 12. 3d].

The infrared spectra of the binary charge transfer complexes namely \( \text{Ni(Hdpd)2-l}_2 \), \( \text{Ni(Hdpd)2-chloranil} \) and \( \text{Ni(Hdpd)2-TCNE} \) are shown (Figure 4). These spectra spectra should be compared with those of \( \text{Ni(Hdpd)2 DDQ, Ni(Hdpd)2 TCNQ} \) and \( \text{Ni(Hdpd)2 TNF} \) where TNF = 2,4,5,7-tetranitro-9-fluorenone published earlier [6], apart from comparing with each other. The intense band in high frequency region (above 2800 cm\(^{-1}\)) of \( \text{Ni(Hdpd)2} \) attributed to hydrogen bonding which is retained in these three complexes. The trend of transmission decreasing at higher frequencies in the region 1700-2800 cm\(^{-1}\) is observed in all of the three complexes indicating that the binary complexes are small band gap semiconductors similar to TCNQ, DDQ and TNF complexes. The nature of transition is analyzed following the equation

\[
\alpha h\nu = B (h\nu-E_g)^r
\]

where \( r = 2 \) or 3 for indirect transitions in disordered materials. These analytical graphs are shown [Figure 12.5]. The other two regions between 1700 and 1000 cm\(^{-1}\) and 400 cm\(^{-1}\) contain broad Gaussian bands in the background absorption. The higher wavenumber Gaussian band is very weak in intensity and asymmetric while the lower wavenumber Gaussian band is very intense and almost symmetric. Almost symmetric absorption envelopes are observed around 1440 cm\(^{-1}\) in the cases of \( \text{l}_2 \) and TCNE complexes. This envelope formation is unclear in the chloranil complex. The Gaussian bands are analyzed for the lowest wave number range [Figure 12.6]. The widths of these Gaussian bands are measures of electron-phonon coupling. Important matters of the binary complexes are summarized [Table 12.1]
Figure 12.4 The infrared spectra of binary CTCs of Ni(Hdpg)$_2$, namely,
(a) Ni(Hdpg)$_2$-I$_2$,
(b) Ni(Hdpg)$_2$-chloranil, and (c) Ni(Hdpg)$_2$-TCNE.
Figure 12.5 Analysis of the nature of transition in binary complexes, namely,

(a) Ni(Hdpg)$_2$-I$_2$, (b) Ni(Hdpg)$_2$-chloranil, and (c) Ni(Hdpg)$_2$-TCNE.
Figure 12.6 Gaussian bands fitted for (a) Ni(Hdpg)2-l2, (b) Ni(Hdpg)2-chloranil, and (c) Ni(Hdpg)2-TCNE.
TABLE 12.1 Absorption Edges of the Binary CTCS of Ni(Hdpg)2

<table>
<thead>
<tr>
<th>Name of the compound</th>
<th>Absorption function</th>
<th>Nature of transition</th>
<th>Value of band gap E(g) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni (Hd pg)(_2)</td>
<td>(\alpha h\nu = (h\nu - E_g)^{1/2})</td>
<td>Allowed direct</td>
<td>0.46 eV</td>
</tr>
<tr>
<td>Ni (Hd pg)(_2)-I(_2)</td>
<td>(\alpha h\nu = (h\nu - E_g)^2)</td>
<td>Allowed indirect</td>
<td>21 eV</td>
</tr>
<tr>
<td>Ni (Hd pg)(_2)-chloranil</td>
<td>(\alpha h\nu = (h\nu - E_g)^2)</td>
<td>Allowed indirect</td>
<td>22 eV</td>
</tr>
<tr>
<td>Ni (Hd pg)(_2)-TCNE</td>
<td>(\alpha h\nu = (h\nu - E_g)^2)</td>
<td>Allowed indirect</td>
<td>23 eV</td>
</tr>
</tbody>
</table>

The nature of transition from the valence to conduction band is found to be similar to that in Ni(Hdpg)\(_2\)-TCNQ, Ni(Hdpg)\(_2\)-DDQ and Ni(Hdpg)\(_2\)-TNF-the binary systems studied earlier [6]. This differs from the transition in purely organic CT complexes which is usually direct being either allowed or forbidden. Only in Ni(Hdpg)\(_2\)-TCNE, there is a break due to a change in the slope of the straight line in \((\alpha h\nu)^{1/2}\) vs \(h\nu\) [plot [Figure 12. 5c)]. This cannot be assigned to absorption \((\alpha_a)\) and emission \((\alpha_e)\) of phonons usually found in an indirect band gap semiconductors in crystalline form due to inverse order of \(\alpha_a\) and \(\alpha_e\) [24]. Also this characteristics cannot be assigned to exciton-phonon coupling leading to either several breaks with intercepts at equal intervals related with transverse optical phonons [25] or curved segments associated with the oscillator absorption functions of phonons when the coupling is strong [26]. The inverted behaviour may be due to the Burstein-Moss shift effect because of the band-filling effect in heavily doped semiconductors or due to excitonic levels within the forbidden gap.

After this interpretation of the spectra of three binary CT complexes based on Ni(Hdpg)\(_2\), we turn on the discussion on the ternary systems namely Ni(Hdpg)\(_2\)-Chloranil-I\(_2\) and Ni(Hdpg)\(_2\)-DDQ-I\(_2\), Ni(Hdpg)\(_2\)-TCNQ-I\(_2\), and Ni(Hdpg)\(_2\)-TCNE-I\(_2\) whose spectra are shown in the full infrared range [Figure 12. 7a, b and 12.10a, 10b] The former two CT complexes involving chloranil and DDQ show two Gaussian envelopes [Figure 12.8a, b and 12.9 a, b]. The TCNQ ternary complex shows two Gaussian bands [Figure 12.11a, b]. The TCNE ternary complex reveals one half-power beta density [Figure 12.12a] envelope indicative of the hopping mechanism of the charge carriers at high energy and one Gaussian-shaped envelope at lower energy [Figure 12.12d].
It is found that the interband transition (intrinsic absorption in a semiconductor) is an allowed indirect transition in the chloranil and DDQ based ternary systems [Figure 12. 8c and 12.9c]. The special character of the complexes lies in the fact that the absorption coefficient should be taken equal to the transmission coefficient (T) as required for the highly conducting materials when the thicknesses of the samples are larger than the penetration depth ($\delta = c/\sqrt{2\pi\mu\sigma}$) even in the band gap region. Thus for the first time that the indirect transition follows the transmission function given by

$$Thv = A(hv - E_g)^r$$

where $r=2$ for chloranil and DDQ complexes and $r=3$ for TCNQ and TCNE complexes [Figure 12. 11c and b] the later arising for the forbidden indirect transitions. We attribute this nature of transition, which is observed for the first time in the experimental studies on semiconductors, to the semimetallic nature of the ternary systems as compared to the binary systems. This type of behaviour in which transmission increases as the wavenumber (or frequency) increases is also found recently in the cases of the binary CT complexes of Ni (N-R-salim)$_2$ where R=H, CH$_3$, C$_2$H$_5$ and C$_6$H$_5$ with standard organic acceptors in which a negative activation energy is also observed in the study of temperature dependence of electrical resistivity [22]. Thus by comparison of spectroscopic features in the band gap region ($hv \geq E_g$), we conclude that the four ternary CT complexes studied presently are semimetals.

More evidence regarding highly electrically conducting nature is based on free-carrier absorption analyzed which reveals scattering of charge carriers by acoustic phonons as found in the cases of three binary CT complexes of Cu(N-H-salim)$_2$ with standard organic acceptors [Figure 12.8d, 12.9d, 12.11d and 12.12c]. The slopes of log $\alpha$ vs log $\lambda$ plots are found to be 1.4, 1.25, 1.64 and 1.4 for the chloranil, DDQ, TCNQ and TCNE complexes, respectively, which should be around 1.5 according to theoretical model [27]. The complexes will be more electrically conducting when acoustic phonons scatter because of the energetically low-lying excitations are acoustic modes as compared to the optical modes and the continuum approximation is also valid for long-wavelength acoustic branches. Even among purely organic charge transfer complexes, the CT complexes which show acoustic

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phonon scattering reveal higher electrical conductivity.

Figure 12.7 The infrared spectra of the ternary CTCs of Ni(Hdpg)\(_2\), namely, (a) Ni(Hdpg)\(_2\) chloranil-I\(_2\), (b) Ni(Hdpg)\(_2\)DDQ-I\(_2\).
Figure 12.8 Analysis of the IR spectrum of Ni(Hdpɡ)2–CA–I2 (a) Gaussian band fitted at lower energy, (b) Gaussian band fitted at higher energy, (c) allowed indirect transition observed in mid-IR range, and (d) free-carrier absorption revealing acoustic phonon scattering.
Figure 12.9 Analysis of the IR spectrum of Ni(Hdpg)₂-DDQ-I₂ (a) Gaussian band fitted at lower energy, (b) Gaussian band fitted at higher energy, (c) allowed indirect transition observed in mid-IR range, (d) free-carrier absorption revealing acoustic phonon scattering.
Figure 12.10 The infrared spectra of the ternary CTCs of Ni(hHdpg)$_2$, namely (a) Ni(Hdpg)$_2$TCNQ-I$_2$ and (b) Ni(Hdpg)$_2$TCNE-I$_2$. 
Figure 12.11 Analysis of the IR spectrum of \( \text{Ni(Hdp)}_2\text{TCNQ}\cdot\text{I}_2 \)

(a) Gaussian band fitted at lower energy
(b) Gaussian band fitted at higher energy
(c) Forbidden indirect transition observed in mid-IR range
(d) Free-carrier absorption revealing acoustic phonon scattering
Figure 12.12 Analysis of the IR spectrum of Ni(Hdpg)$_2$-TCNE-I$_2$

(a) half power beta density fitted at higher energy
(b) forbidden indirect transition observed in mid-IR range
(c) free-carrier absorption revealing acoustic phonon scattering
(d) Gaussian band fitted at lower energy
TABLE 12.4 Summary of Gaussian Distributions in the Infrared Spectra of Ni (Hdpg)$_2$ and Its Binary as Well as Ternary Complexes

<table>
<thead>
<tr>
<th>Name of compound</th>
<th>Central wave number (cm$^{-1}$) (eV)</th>
<th>Absorption maximum (%)</th>
<th>FWHM (cm$^{-1}$) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni (Hdmg)$_2$</td>
<td>1380 (0.1710)</td>
<td>3.0</td>
<td>600 (0.075)</td>
</tr>
<tr>
<td>Ni (Hdpg)$_2$</td>
<td>1330 (0.1660)800(0.10)</td>
<td>3.5 8</td>
<td>300 (0.0375)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>400 (0.05)</td>
</tr>
<tr>
<td>Ni (Hdpg)$_2$−I$_2$</td>
<td>900 (0.1125)</td>
<td>3.0</td>
<td>600 (0.075)</td>
</tr>
<tr>
<td>Ni (Hdpg)$_2$−chloranil</td>
<td>800 (0.10)</td>
<td>7.0</td>
<td>600 (0.075)</td>
</tr>
<tr>
<td>Ni (Hdpg)$_2$−TCNE</td>
<td>800 (0.10)</td>
<td>8.0</td>
<td>600 (0.075)</td>
</tr>
<tr>
<td>Ni (Hdpg)$_2$ Chloranil I$_2$</td>
<td>1400 (0.175)800 (0.10)</td>
<td>6.0 8</td>
<td>800 (0.10)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>470 (0.06)</td>
</tr>
<tr>
<td>Ni (Hdpg)$_2$−DDQ I$_2$</td>
<td>1450 (0.18) 800 (0.10)</td>
<td>4.0 9</td>
<td>640 (0.08)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>500 (0.005)</td>
</tr>
<tr>
<td>Ni (Hdpg)$_2$−TCNQ I$_2$</td>
<td>1380 (0.17) 800 (0.10)</td>
<td>5.0 8</td>
<td>840 (0.105)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>500 (0.025)</td>
</tr>
<tr>
<td>Ni (Hdpg)$_2$−TCNE−I$_2$</td>
<td>780 (0.0975)</td>
<td>11.0</td>
<td>500 (0.0625)</td>
</tr>
</tbody>
</table>

12.4 CONCLUSIONS:
The spectral study of Ni(Hdpg)$_2$ complexes—both binary and ternary—has shown the electrically conducting nature of the complexes; binary ones being small band-gap semiconducting while ternary ones being semimetallic with small but negative band-gaps. It is established that the charge transfer complexes based on metal chelate as one of the components are more conducting than the ternary complexes of purely organic donors and acceptors. This is consistent with the superconducting properties found in some of the ternary complexes based on metal complex ions at low temperatures.

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Reference

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