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Spectroscopic Study of Ternary CT Complexes Based on the Organometallic Donor – Bis(Diphenylglyoximato)Ni^{II}

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The infrared spectra of the ternary complexes based on the organometallic chelate, namely, bis(N-diphenylglyoximato) Ni^{II} working as an electron donor with standard organic acceptors like TCNQ, TCNE, chloranil, and DDQ have been studied for the first time keeping iodine as common acceptor for the four complexes. It is found that binary complexes of Ni $(Hdpg)_2$ are semiconductors while the four ternary complexes exhibit semimetallic behavior. However, in chloranil and DDQ complexes, this modification is not as pronounced as observed in TCNQ and TCNE complexes.

Keywords: binary and ternary complexes; direct and indirect transition; free-camer absorption; Gaussian bands; infrared spectra

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

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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 semimetallic 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 semimetallic nature on the bases of their spectroscopic study.

EXPERIMENTAL

The three binary complexes, namely, $Ni(Hdpg)_2$–$I_2Ni(Hdpg)_2$-TCNE and $Ni(Hdpg)_2$–chloranil where TCNE = tetraycyano 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-I_2, $Ni(Hdpg)_2$-TCNE-I_2, $Ni(Hdpg)_2$-Chloranil-I_2, and $Ni(Hdpg)_2$-DDQ-I_2 were prepared where 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 pastle 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 prepared—using 95% spectrograde KBr powder which was moisture-free and 5% of the binary and ternary complexes.

RESULTS AND DISCUSION

The molecular structures of $Ni(Hdpg)_2$ and organic acceptors used in the present study are shown (Fig. 1). The infrared spectra of $Ni(Hdpg)_2$—the methyl analog and $Ni(Hdpg)_2$ are shown for comparison (Fig. 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 $Ni(Hdpg)_2$ (Fig. 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-salicyldiminato)Ni^{II}

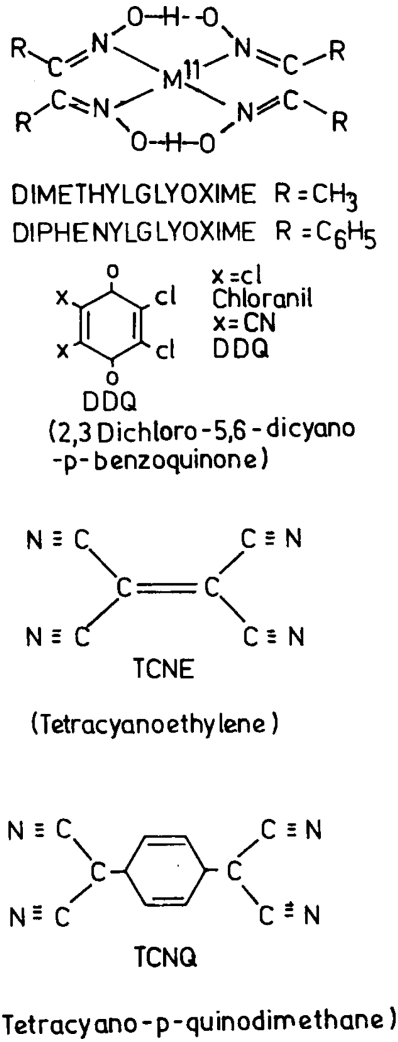

FIGURE 1 Molecular structures of two metal dioximes and organic acceptors.

where R = H_1 CH_3, C_2H_5, and C_6H_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 band but broader and asymmetric with high energy tail. This Gaussian band is centered

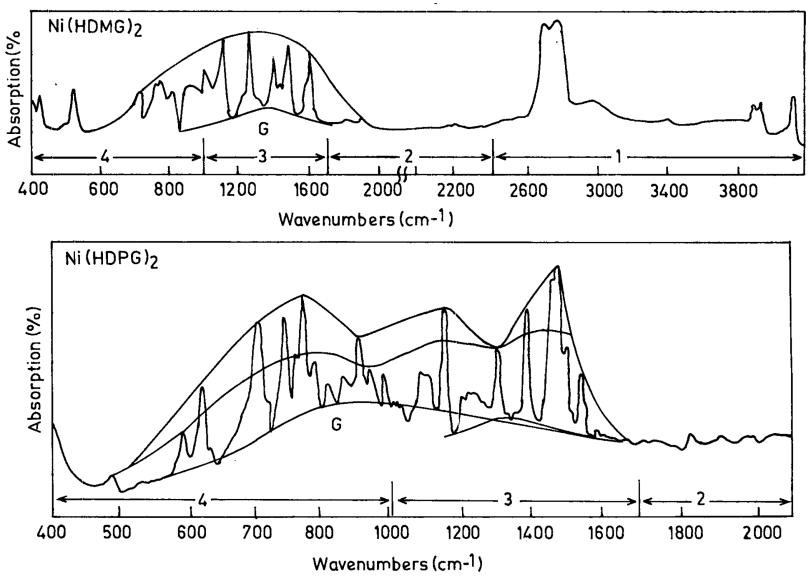

FIGURE 2 Infrared spectra of (a) $Ni(Hdmg)_2$ and (b) $Ni(Hdpg)_2$.

around $3500\,cm^{-1}$ (Fig. 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 $Ni(Hdpg)_2$ (Fig. 3).

The comparison between the spectra of $Ni(Hdmg)_2$ and $Ni(Hdpg)_2$ indicates a reduction in absorption in the phenyl dioximate with increasing the nickel-nickel distance to 3–52 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 the 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 π-clouds increases the intermolecular distance in $Ni(Hdpg)_2$ but nickel ion is chemically reduced

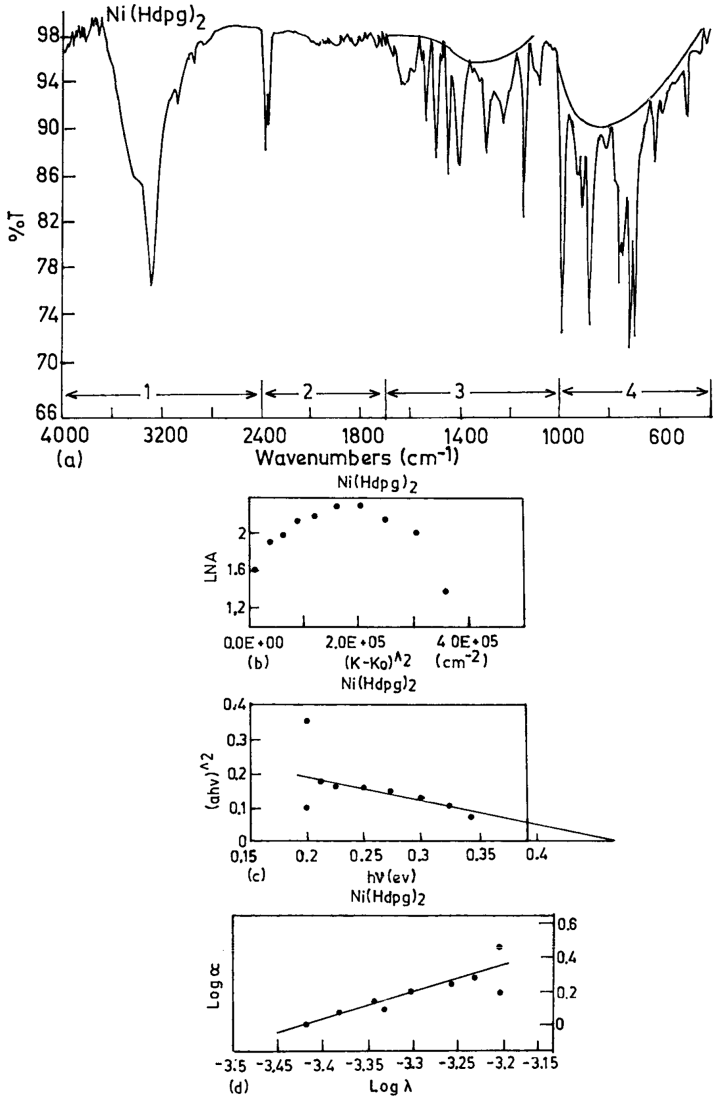

FIGURE 3 (a) IR spectrum of $Ni(Hdpg)_2$; (b) one of the Gaussian bands fitted from the spectrum; (c) direct transition observed in the IR range; and (d) verification of Acoustic phonon scattering.

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 (Fig. 3b). The widths of the Gaussian bands are determined by electron-phonon interactions. However, the maximum absorption (α_{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 (Fig. 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 $E_g \cong 0.46$ 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 (Fig. 3c).

The final analysis of free-carrier absorption is carried out to plot log α vs log λ and the slope reveals scattering of electrons by acoustic phonons in the range $h\nu > E_g = 0.2$ eV. This shows that the conduction band is stabilized in the direction transverse to metal chains (Fig. 3d).

The infrared spectra of the binary charge transfer complexes namely Ni(Hdpg)$_2$-I$_2$, Ni(Hdpg)$_2$-chloranil, and Ni(Hdpg)$_2$-TCNE are shown (Fig. 4). These spectra spectra should be compared with those of Ni(Hdpg)$_2$ DDQ, Ni(Hdpg)$_2$ TCNQ and Ni(Hdpg)$_2$ 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 Ni(Hdpg)$_2$ is 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

$$\alpha h\nu = B(h\nu - E_g)^r,$$

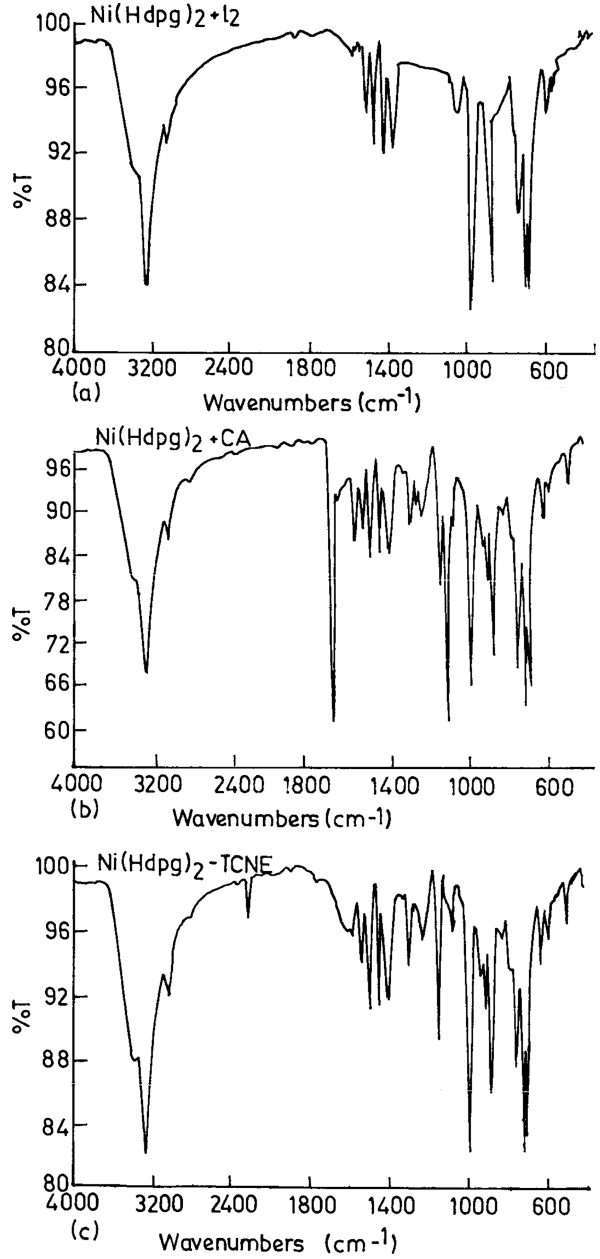

FIGURE 4 The infrared spectra of binary CTCs of $Ni(Hdpg)_2$, namely, (a) $Ni(Hdpg)_2$-I_2, (b) $Ni(Hdpg)_2$-chloranil, and (c) $Ni(Hdpg)_2$-TCNE.

where r = 2 or 3 for indirect transitions in disordered materials. These analytical graphs are shown (Fig. 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 I_2 and TCNE complexes. This envelope formation is unclear in the chloranil complex. The Gaussian bands are analyzed for the lowest wavenumber range (Fig. 6). The widths of these Gaussians

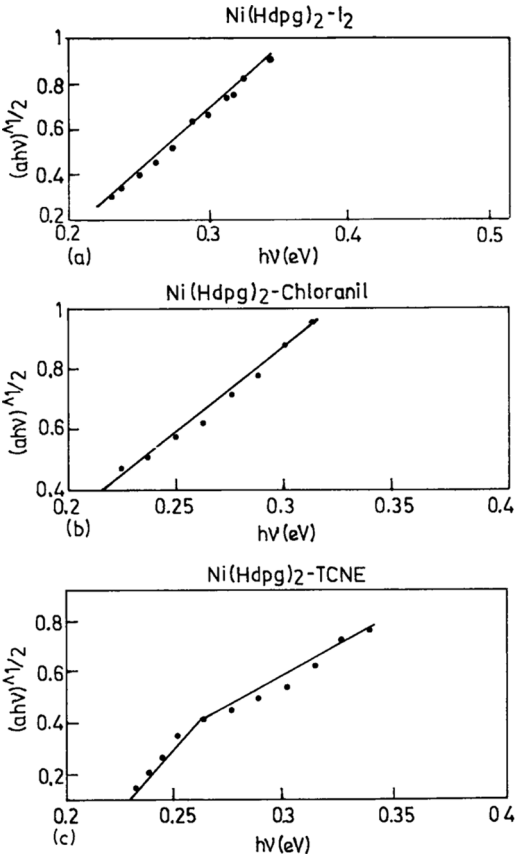

FIGURE 5 Analysis of the nature of transition in binary complexes, namely, (a) Ni(Hdpg)$_2$-I_2, (b) Ni(Hdpg)$_2$-chloranil, and (c) Ni(Hdpg)$_2$-TCNE.

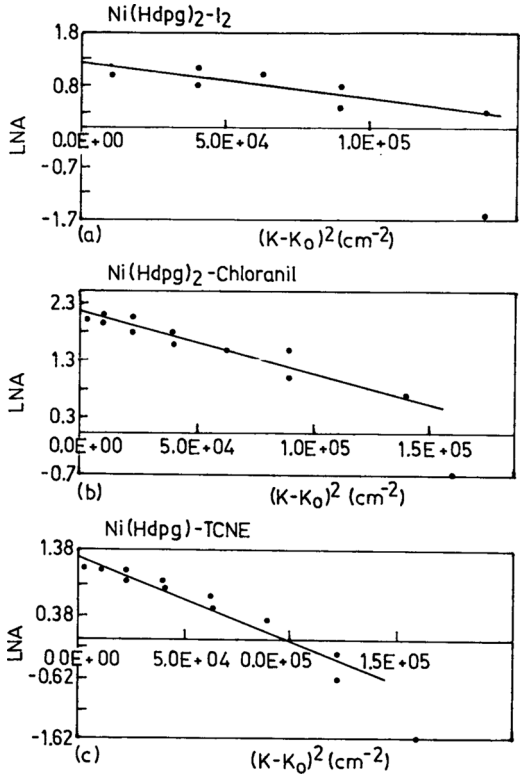

FIGURE 6 Gaussian bands fitted for (a) $Ni(Hdpg)_2$-I_2, (b) $Ni(Hdpg)_2$-chloranil, and (c) $Ni(Hdpg)_2$-TCNE.

are measures of electron-phonon coupling. Important matters of the binary complexes are summarized (Table 1).

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,

TABLE 1 Absorption Edges of the Binary CTCS of $Ni(Hdpg)_2$

Name of the compound	Absorption function	Nature of transition	Value of band gap Eg (eV)
Ni (Hd pg)$_2$	$\alpha h\upsilon = (h\upsilon - Eg)^{1/2}$	Allowed direct	0. 46 eV
Ni (Hd pg)$_2$–I_2	$\alpha h\upsilon = (h\upsilon - Eg)^{2}$	Allowed indirect	0. 21 eV
Ni (Hd pg)$_2$–chloranil	$\alpha h\upsilon = (h\upsilon - Eg)^{2}$	Allowed indirect	0. 22 eV
Ni (Hd pg)$_2$–TCNE	$\alpha h\upsilon = (h\upsilon - Eg)^{2}$	Allowed indirect	0. 23 eV

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 $(\alpha h\nu)^{1/2}$ versus $h\nu$ [plot (Fig. 5c)]. This cannot be assigned to absorption (α_a) and emission (α_e) of phonons usually found in an indirect band gap semiconductors in crystalline form due to inverse order of α_a and α_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 couplings are strong [26]. The inverted behavior 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 7a,b and 10a,b). The former two CT complexes involving chloranil and DDQ show two Gaussian envelopes (Figure 8a,b and 9a,b). The TCNQ ternary complex shows two Gaussian bands (Figure 11a, b). The TCNE ternary complex reveals one half-power beta density (Fig. 12a) envelope indicative of the hopping mechanism of the charge carriers at high energy and one Gaussian-shaped envelope at lower energy (Fig. 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 (Figs. 8c and 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 ($\delta = c/\sqrt{2\pi\omega\mu\sigma}$) even in the band gap region. Thus for the first time that the indirect transition follows the transmission function given by

$$Th\nu = A(h\nu - E_g)^r,$$

where r = 2 for chloranil and DDQ complexes and r = 3 for TCNQ and TCNE complexes (Figs. 11c and 12b), 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

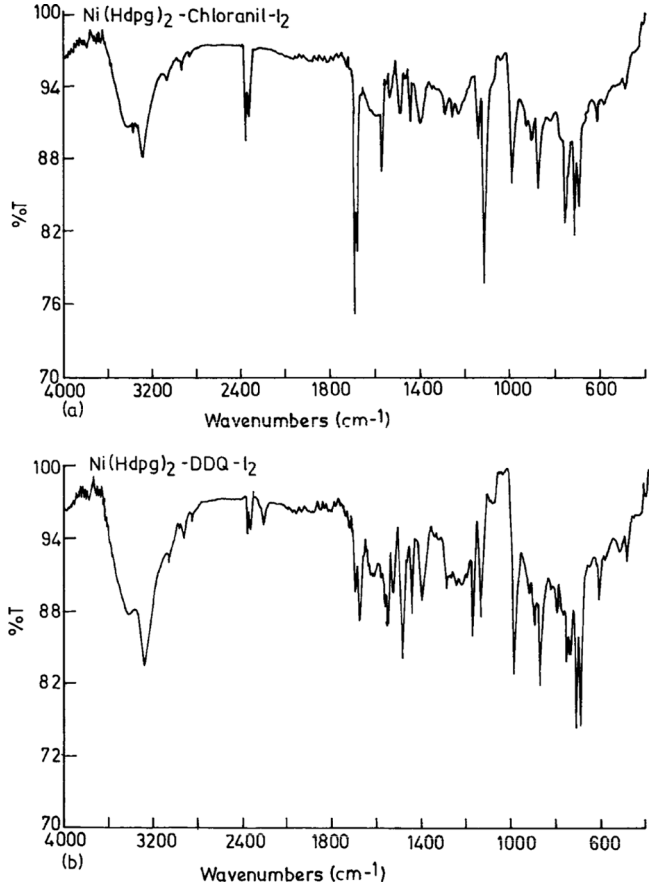

FIGURE 7 The infrared spectra of the ternary CTCs of $Ni(Hdpg)_2$, namely, (a) $Ni(Hdpg)_2$ chloranil-I_2, (b) $Ni(Hdpg)_2$DDQ-I_2.

compared to the binary systems. This type of behavior 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_2H_5, and C_6H_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 ($h\nu \geq E_g$), we conclude that the four ternary CT complexes studied presently are semimetals.

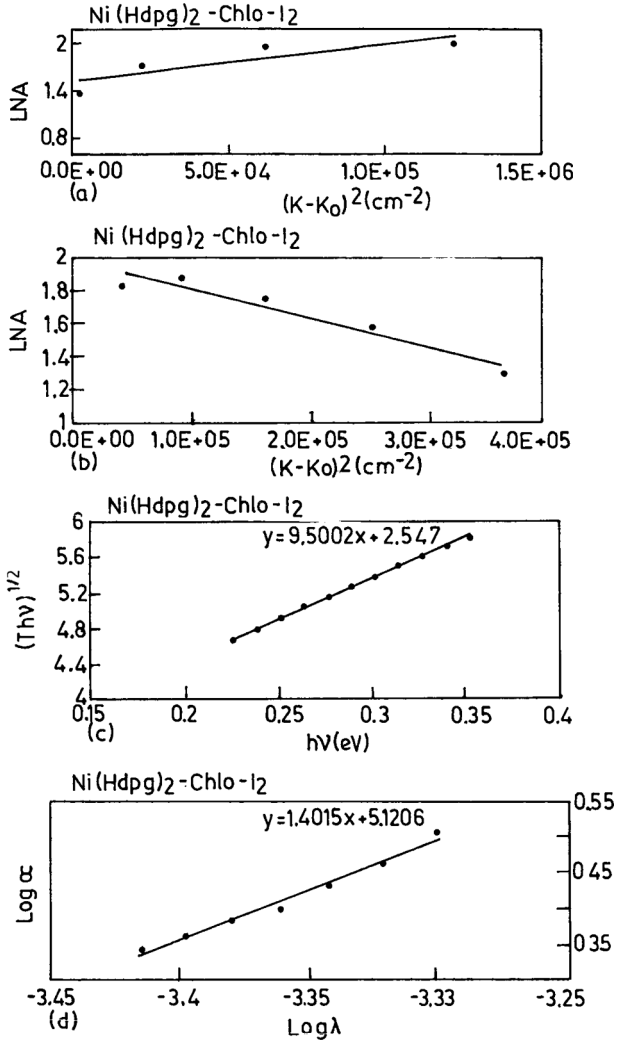

FIGURE 8 Analysis of the IR spectrum of Ni(Hdpg)$_2$–CA–I_2 (a) Gaussian band fitted at lower energy, (b) Gaussian band fitted at higher energy, (c) allowed indirect transition observed in mid-IR range, and (d) free-carrier absorption revealing acoustic phonon scattering.

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

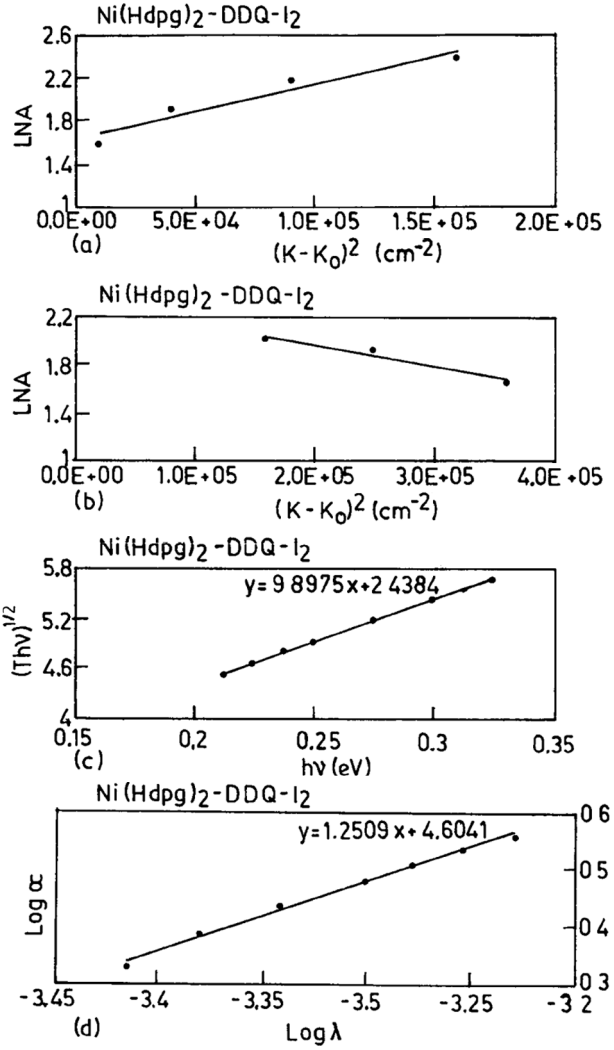

FIGURE 9 Analysis of the IR spectrum of Ni(Hdpg)$_2$-DDQ-I$_2$ (a) Gaussian band fitted at lower energy, (b) Gaussian band fitted at higher energy, (c) allowed indirect transition observed in mid-IR range, (d) free-carrier absorption revealing acoustic phonon scattering.

acceptors (Figs. 8d, 9d, 11d and 12c). The slopes of log α *versus* log λ plots are found to be 1.4, 1.25, 1.64, and 1.4 for the chloranil, DDQ, TCNQ, and TCNE ternary complexes, respectively, which should be

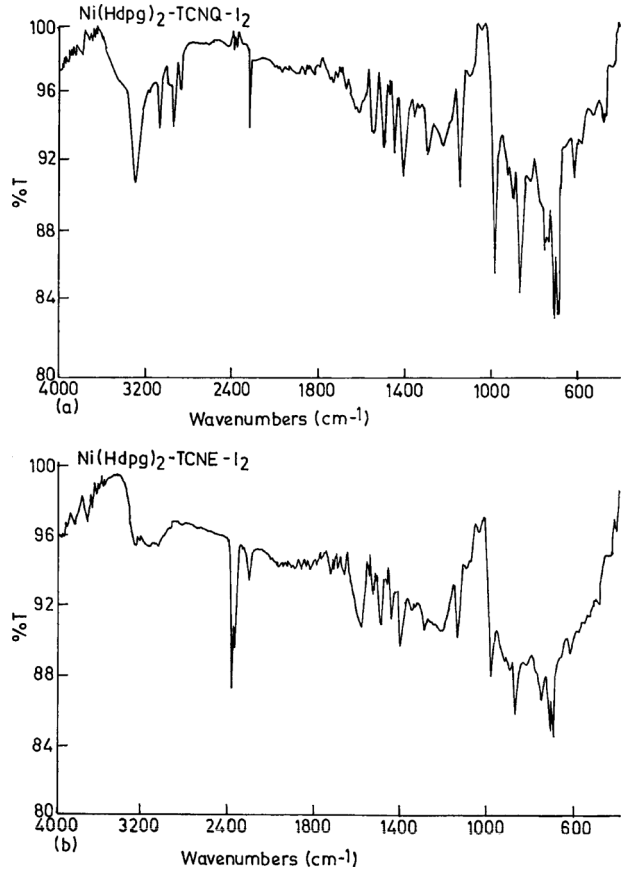

FIGURE 10 The infrared spectra of the ternary CTCs of $Ni(Hdpg)_2$, namely, (a) $Ni(Hdpg)_2TCNQ\text{-}I_2$ and (b) $Ni(Hdpg)_2\text{-}TCNE\text{-}I_2$.

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 exitations 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 phonon scattering reveal higher electrical conductivity.

The absorption edges of Ni $(Hdpg)_2$ and its binary CT complexes are summarized (Table 1). Similar mid – IR edges of ternary CTCS of Ni $(Hdpg)_2$ are also summarized in terms of basic parameters (Table 2).

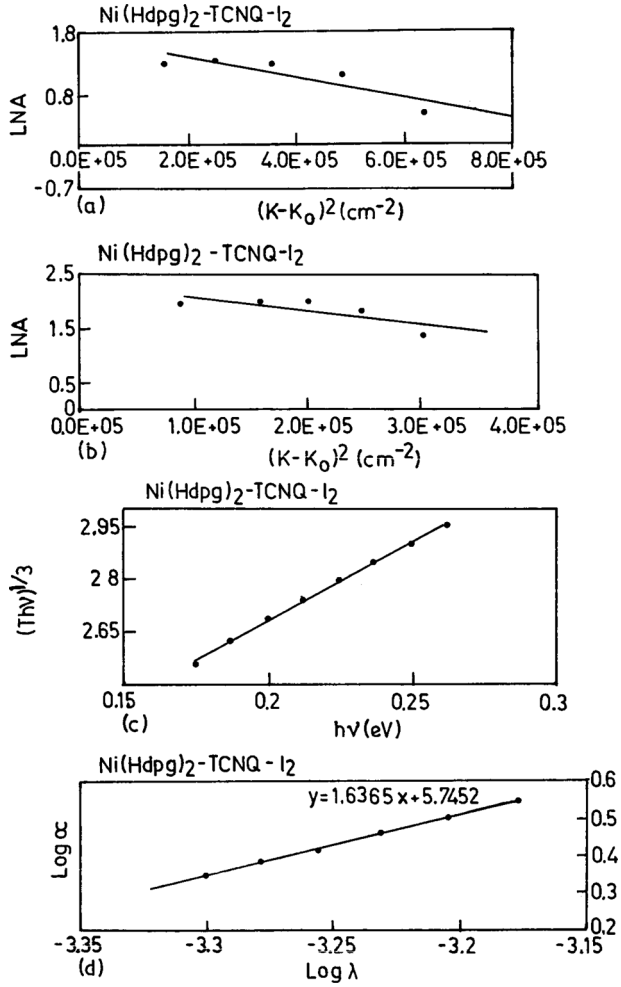

FIGURE 11 Analysis of the IR spectrum of Ni(Hdpg)$_2$-TCNQ-I$_2$ (a) Gaussian band fitted at lower energy, (b) Gaussian band fitted at higher energy, (c) forbidden indirect transition observed in mid-IR range, (d) free-carrier absorption revealing acoustic phonon scattering.

The exponents of the power law of free-carriers are tabulated (Table 3) and it is concluded that the charge carriers are scattered by acoustic phonons. The parameters of the Gaussian distributions found in the infrared spectra of all the materials studied in the present work are tabulated (Table 4).

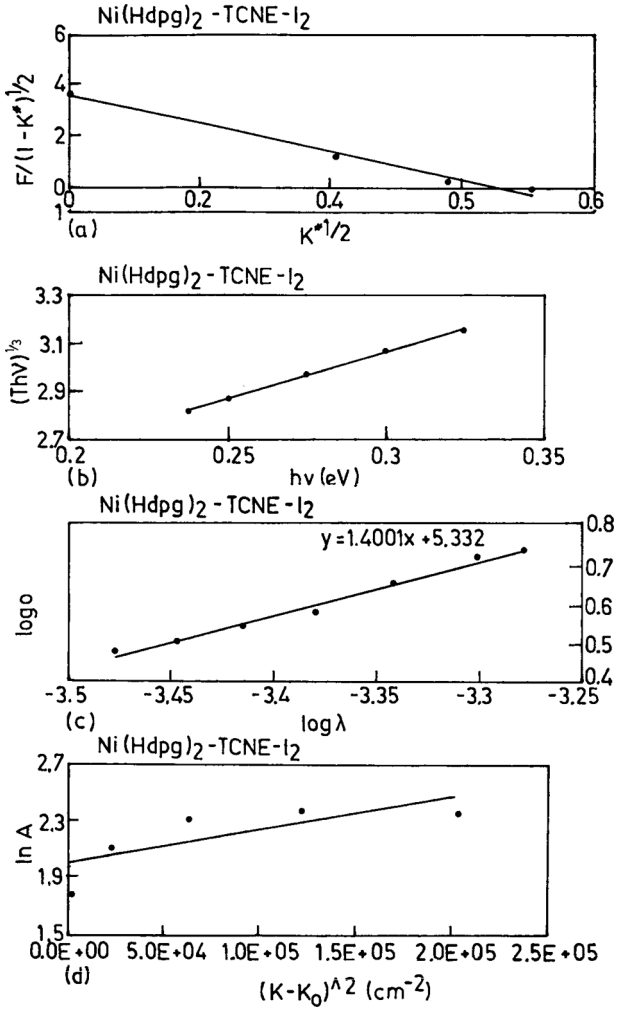

FIGURE 12 Analysis of the IR spectrum of Ni(Hdpg)$_2$-TCNE-I$_2$ (a) half power beta density fitted at higher energy, (b) forbidden indirect transition observed in mid-IR range, (c) free-carrier absorption revealing acoustic phonon scattering, (d) Gaussian band fitted at lower energy.

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

TABLE 2 Absorption Edges of the Ternary CTCS of Ni (Hd pg)$_2$

Name of the CTC	Absorption function	Nature of transition	Value of band gap Eg (eV)
Ni (Hdpg)$_2$–chloranil $_$ I$_2$	$\alpha h\upsilon = (h\upsilon - Eg)^2$	Allowed indirect	0. 225
Ni (Hdpg)$_2$–DDQ $_$ I$_2$	$\alpha h\upsilon = (h\upsilon - Eg)^2$	Allowed indirect	0. 215
Ni (Hdpg)$_2$–TCNQ $_$ I$_2$	$\alpha h\upsilon = (h\upsilon - Eg)^3$	Forbidden indirect	0. 175
Ni (Hdpg)$_2$–TCNE $_$ I$_2$	$\alpha h\upsilon = (h\upsilon - Eg)^3$	Forbidden indirect	0. 23

TABLE 3 Free Carrier Absorption of Ternary CTCs of Ni (Hdpg)$_2$

Name of the CTC	Slope of log α versus log λ	Scatterers of charge carriers
Ni (Hdpg)$_2$	1. 60	Acoustic phonons
Ni (Hdpg)$_2$–chloranil $_$ I$_2$	1. 40	Acoustic phonons
Ni (Hdpg)$_2$–DDQ $_$ I$_2$	1. 25	Acoustic phonons
Ni (Hdpg)$_2$–TCNQ $_$ I$_2$	1. 64	Acoustic phonons
Ni (Hdpg)$_2$–TCNE $_$ I$_2$	1. 40	Acoustic phonons

TABLE 4 Summary of Gaussian Distributions in the Infrared Spectra of Ni (Hdpg)$_2$ and Its Binary as Well as Ternary Complexes

	Basic parameters of the Gaussian distributions		
Name of compound	Central wave number (cm^{-1}) (eV)	Absorption maximum (%)	FWHM (cm^{-1}) (eV)
Ni (Hdmg)$_2$	1380 (0. 1710)	3. 0	600 (0. 075)
Ni (Hdpg)$_2$	1330 (0. 1660) 800 (0. 10)	3. 5 8	300 (0. 0375)
			400 (0. 05)
Ni (Hdpg)$_{2-12}$	900 (0. 1125)	3. 0	600 (0. 075)
Ni (Hdpg)$_2$–chloranil	800 (0. 10)	7. 0	600 (0. 075)
Ni (Hdpg)$_2$–TCNE	800 (0. 10)	8. 0	600 (0. 075)
Ni (Hdpg)$_2$ Chloranil $_$ I$_2$	1400 (0. 175) 800 (0. 10)	6. 0 8	800 (0. 10)
			470 (0. 06)
Ni (Hdpg)$_2$–DDQ $_$ I$_2$	1450 (0. 18) 800 (0. 10)	4. 0 9	640 (0. 08)
			500 (0. 005)
Ni (Hdpg)$_2$–TCNQ $_$ I$_2$	1380 (0. 17) 800 (0. 10)	5. 0 8	840 (0. 105)
			500 (0. 025)
Ni (Hdpg)$_2$–TCNE $_$ I$_2$	780 (0. 0975)	11. 0	500 (0. 0625)

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 [28]. 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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