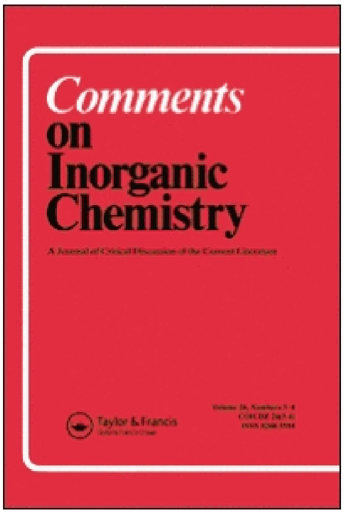

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# New Symmetrical and Unsymmetrical Nickel-Dithiolene Complexes Useful as Near-IR Dyes and Precursors of Sulfur-Rich Donors

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# New Symmetrical and Unsymmetrical Nickel-Dithiolene Complexes Useful as Near-IR Dyes and Precursors of Sulfur-Rich Donors

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Novel symmetrical and unsymmetrical nickel dithiolene complexes based on a new ligand $R_2$timdt (the −1 charged 1,3-dialkylimidazolidine-2,4,5-trithione) and dmit or mnt (dmit = 2-thioxo-1,3-dithiole-4,5-dithiolate; mnt = maleonitriledithiolate) useful as NIR-dyes and electrochromic materials in the 880–1400 nm region are described here. The $R_2$ timdt ligand, where N-electron donor atoms of the imidazoline ring are forced into co-planarity with the dithiolene ring, revealed to be valuable in shifting the low energy transition typical of this class of complexes in a region of remarkable interest for near-IR dyes, while stability was maintained. The symmetrical neutral complexes absorb very strongly at approximately 1000 nm, region of special interest for NIR-dyes in order to be used in Q-switching Neodymium lasers, which operate at 1064 nm. Moreover these complexes work as switchable NIR-dyes, since the absorption is shifted to approximately 1400 nm on reversible reduction. In the unsymmetrical nickel-dithiolene complexes involving both the $Pr^i_2$timdt and dmit or mnt ligands a tuning of the NIR-absorption depending on the combination of the ligands and of the charge is achieved.

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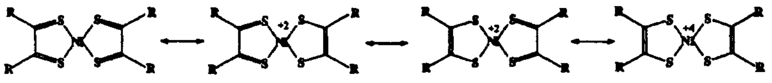
Moreover the peculiar behaviour of the symmetrical complexes to work as precursors of sulfur-rich donors, which are not easily to obtain by conventional routes and are of interest in coordination chemistry, in the field of charge-transfer adducts and of anticancer agents, is also described.

Keywords: *NIR-dyes; electrochromism; nickel-dithiolenes; sulfur-donors*

## 1. INTRODUCTION

Interest in metal-dithiolene complexes is due to the unique chemical nature related to their non-classical electronic structure and to their applications in the field of new molecular materials. Solids that exhibit electrical[1] and magnetic properties,[2] near-infrared dyes,[3] non-linear optical materials[4] based on metal-dithiolenes have been obtained. A qualitative description of the bonding in neutral square-planar nickel-dithiolenes involves a resonance hybrid of limiting structures in which the metal assumes formal oxidation states 0, +2, +4 and the ligands work as neutral dithioketones (**1**), dithioketone-dithiolate (**2**), dithiolates (**3**), as shown below.



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The high degree of electron-delocalization that includes the metal producing cyclic delocalization (aromaticity), is responsible for an intense electronic transition at low energies ($\lambda_{max}$>700 nm), assigned to a $\pi \rightarrow \pi^*$ ($b_{1u} \rightarrow b_{2g}$) transition between the HOMO and the LUMO,[5] that makes these complexes suitable to be used as near-infrared dyes.

Square-planar nickel-dithiolenes are capable to exist in different oxidation states, with different NIR-absorptions, and these states are connected through reversible redox steps. In the monoanionic form a bathochromic shift of the absorption, while in the dianionic form a bleaching are expected, because the formerly defined LUMO becomes half-filled and filled respectively.[6] Chemical species which can be electronically switched between two "colours" or which undergo a colour change between a coloured state and a bleached state are called electrochromic materials and are now attracting much attention with the view to obtain optical devices for optical information and storage.[7]

While the basic chemical properties of metal-dithiolenes are quite well established since late sixties, as shown by the review article by McCleverty[8] that contains valuable information still topical, this field is into expanding development in order to address the preparation of metallo-dithiolenes with tailored properties for the various cited applications.

Among the several potential applications of nickel-dithiolenes as NIR-dyes (for example for encoding paper money bills) Drexhage and Mueller-Westerhoff discovered since the early seventies that these complexes can be used in Q-switching* infrared lasers.[9] The absorption maximum of the NIR-dyes is required as closely as possible to the laser wavelength and also an appropriate excited state lifetime, good solubility (the dye is used in solution) and high thermal and photochemical stability to the laser wavelength are required.

Among the lasers operating in the NIR-region the Nd-lasers operate at 1064 nm and beyond this wavelength the iodine and erbium operate at 1310 and 1540 nm respectively. The iodine and neodymium lasers are very dangerous to the human eye, so the search for suitable dyes in the 1000- 1350 nm region is also important for obtaining protective filters.

As a result of an extensive experimental and theoretical investigation, Mueller-Westerhoff's group established criteria useful for a rational synthesis of these complexes. It has been shown that donor substituents in the parent dithiolene $[Ni(edt)_2]$ (edt = ethylenedithiolate) raise the energy of the HOMO more than that of the LUMO and a consequent shift of the low-energy band to lower frequencies is produced, and that donor substituents fixed in coplanarity with the dithiolene moiety give the best results to achieve low-frequency shifts and increase in the extinction coefficients. However donor substituents that should give rise to a strong shift to lower frequencies, can also force the HOMO to

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* The Q-switching term refers to a change in the "Quality" of a resonator cavity. The Q-switching is achieved introducing a shutter (the dye in solution) into the cavity between the laser and the output-medium. The shutter suppresses photons which stimulate the emission while the laser medium is still being pumped by the laser source. The photon flux will eventually reach a level at which the dye can not return to the ground state fast enough to maintain absorption. Thus the dye will temporarily bleach out and the lasing occurs in the form of a very powerful pulse, due to the high population inversion reached. The dye, being a reversibly bleachable absorber, works as a shutter which does not need external mechanical control units.

become antibonding. Consequently, an induced undesirable increased reactivity leading to the loss of one or two electrons may be observed. The direct preparation of stable dicationic dithiolenes by using 1,4-dimethyl-piperazine-2,3-dithione ($Me_2$pipdt), where the N-donor atoms are adjacent to the dithiolene moiety, useless as NIR-dyes, is in agreement with these predictions.[6] To generate the desired shifts while maintaining stability of the complexes Mueller-Westerhoff used the combination of a coplanar $\pi$-system linked to the dithiolene core and the presence of donor substituents on the ligand (not adjacent to the dithiolene core) as the best compromise.

In spite of the presence of the N-donor atoms adjacent to the dithiolene core, the new class of symmetrical and unsymmetrical (or mixed-ligand) nickel-dithiolenes based on a new ligand $R_2$timdt (the $-1$ charged 1,3-dialkylimidazolidine-2,4,5-trithione) are isolable both in the neutral and in the monoreduced form and exhibit relevant properties as NIR-dyes. In fact the symmetrical neutral complexes show the expected absorption at approximately 1000 nm, close to the emission frequency of Neodymium lasers, with a remarkably high absorption coefficient ($\varepsilon = 78000$ $dm^3$ $mol^{-1}$ $cm^{-1}$, to our knowledge the higher value still achieved). These properties coupled with their high thermal and photochemical stability at the laser wavelength, add interest for an application of these materials as NIR dyes in Q-switching Neodymium lasers.[10] In the "unsymmetrical" nickel-dithiolene complexes bearing both the $Pr^i_2$ timdt ($Pr^i$ = propyl-*iso*) and dmit (dmit = 2-thioxo-1,3-dithiole-4,5-dithiolate) or mnt (mnt = maleonitriledithiolate) ligands a tuning of the NIR-absorption depending on the combination of the ligands is achieved.[11] A significant bathochromic shift of this absorption is also achieved in their monoreduced derivatives.

Moreover the peculiar behaviour of these complexes as precursors of new sulfur-rich donors which are not easily obtained by conventional synthetic methods, and are of interest in coordination chemistry, in the field of charge-transfer adducts and of anticancer agents is described.

## 2. SYMMETRICAL NICKEL-DITHIOLENES: $[Ni(R_2timdt)_2]$

The symmetrical derivatives[12,13] are prepared by the *in situ* sulfurization reaction of the 1,3-dialkylimidazolidine-2-thione-4,5-dione (**4**) in the presence of the metal according to Scheme 2.1. The foreseen 1,3-dialkylimidazolidine-2,4,5-trithione (**I**) and its monoreduced form ($R_2$timdt) have never been isolated as free ligands. In fact the sulfurization of **4**, in the absence of the metal, produces 4,5,9,10-tetrathiocino[1,2-*b*:5,6-*b*′]diimidazolyl-1,3,8,10-tetraalkane-2,7-dithiones $R_4$todit (**5**).[14] ($Pr^i_2$timdt)$_2$ (**6**), an isomer of **5**, is obtained in trace amounts when R is the bulky $Pr^i$ group.[10b*]

The sulfurization of **4**, in the presence of $NiCl_2{\cdot}6H_2O$, produces [Ni($R_2$timdt)$_2$] **7** in low yields. Significant improvement in the yields (from 10 to 40% approximately) is obtained when using Ni powder instead of the salt. The derivatives with R= Me, Et, $Pr^i$, Bu, $Bu^i$, $Pe^i$, Hex, Hep, Dec, Dod have been prepared.[18] These complexes exhibit the Near-IR absorption approximately at the same wavelength ($\lambda$=1001–1004 nm, $\varepsilon$ =76000–78000 $dm^3\ mol^{-1}cm^{-1}$), showing that the R-substituents on the N-atoms do not significantly affect the transition.

In **Figure 2.1** a typical spectrum of the $CHCl_3$ solution of the R= $Pr^i$ derivative is reported.

Recently several square-planar metal dithiolenes derived from R,R'timdt have been prepared on varying the metal (M(II)=Ni, Pd, Pt) and substituents.[19] As previously found, only slight shifts are observed on changing substituents R and R′. Aromatic substituents produce the higher shifts in the wavelength of absorption (~ 10–15 nm). On variation of the metal, while Ni- and Pt-complexes absorb at approximately the same wavelength, the Pd-derivative undergoes a slight shift in the wavelength of absorption (~20 nm). Shifts of the absorption maximum are also achievable by variation of the solvent, since $\lambda_{max}$ is solvent-dependent (solvatochromism).[20] Many attempts to correlate the position of electronic absorption bands with the polarity of the solvent have been done. The solvent dependence of the wavelength of the absorption of light is related to the stabilization of the ground-state and excited states by intermolecular forces which can affect the transition

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* The reason why five-membered cyclic dithiooxamides can not be obtained, while six-membered cyclic dithiooxamides are prepared by this way, is not well understood.[15] The only well characterized five-membered rings containing a dithiooxamide group are 1,1-dimethyl-2,5-bis(chlorodimethylsylil)-1-sila-2,5-diazacyclopentane-3,4-dithione and similar compounds.[16] The capability of imidazole ring to give rise to C-C coupling between the rings similar to what happens in the sulfurization reaction of **4** which produces **5**, has been also observed when reacting 1-methylimidazole (MeIm) with elemental sulfur to produce a dianion formed through the 4,4′-coupling of two MeIm rings, the remaining four CH centers being converted to thiocarbonyls.[17]

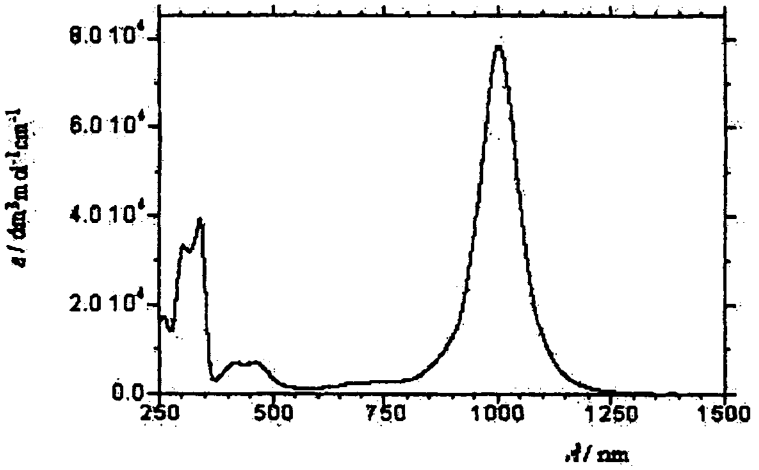
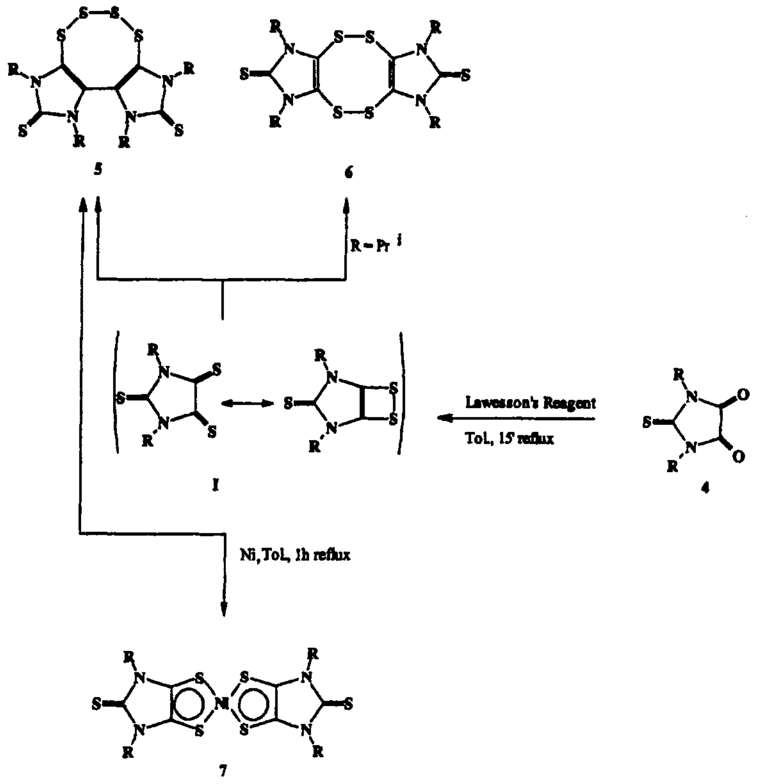


FIGURE 2.1 UV-VIS-NIR spectrum of 7 in $CHCl_3$ solution

energies. Several properties of the solvent (depending on Coulomb, directional, inductive, dispersion, charge-transfer, hydrogen-bonding forces) contribute to the solvation behaviour of a solvent, thus it is not possible to correlate solvatochromism by a single property.[20a,b] Positive solvatochromism (a bathochromic shift as the polarity of the solvent increases) has been observed for $[Ni(4\text{-}DAMB)_2]$ (4-DAMB= 4-dimethylaminodithiobenzyl).[20d] This result is unforeseen due to the nature of the electronic transition involved. The nature of the NIR-peak is quite well established for square-planar nickel dithiolenes. Molecular orbital calculations, both semiempirical and more sophisticated *ab-initio*, agree in assign this absorption to a $\pi \rightarrow \pi^*$ ($b_{1u} \rightarrow b_{2g}$) transition between the HOMO and the LUMO mainly located at the ligand (a $3d_\pi$-type orbital of the nickel ion contributes to the LUMO to a minor extent).[5,19] For $\pi \rightarrow \pi^*$ transitions in dipole free compounds a red-shift with increasing refractive index of the solvent (dispersion forces depend on the polarizability and hence on the refractive index) is expected.[20b] The blue-shift for $[Ni(4\text{-}DAMB)_2]$ has been explained in therms of a change in symmetry of the complex on increase in donor number of the solvent.[20d] However experimental evidence (EPR spectra, comparison of electronic spectra with those of the mono-reduced complex) suggests that the for-



SCHEME 2.1

mation of the monoanion rather than solvation effects is responsible for the observed spectral changes.

We have instead observed a negative solvatochromism of the NIR-peak for 7 ($\lambda_{max}$= 986, 1002 and 1042 nm in $CH_3CN$, THF and $CS_2$ respectively). It seems reasonable to ascribe the observed trend of $\lambda_{max}$ for 7 to dispersion forces, even though a deeper investigation involving also a reinvestigation of literature data is required to support these findings.

It is noteworthy that the intensity of the NIR-absorption in **7** is approximately double than that the highest value found for literature nickel-dithiolene complexes ($\varepsilon$=15000 to 40000 dm$^3$ mol$^{-1}$ cm$^{-1}$).

The properties of these very promising NIR-dyes are ascribed to the achievement of a dithiolene containing nitrogen atoms adjacent to the dithiolene core but fixed into coplanarity in the imidazoline-ring where extensive $\pi$-delocalization exists.

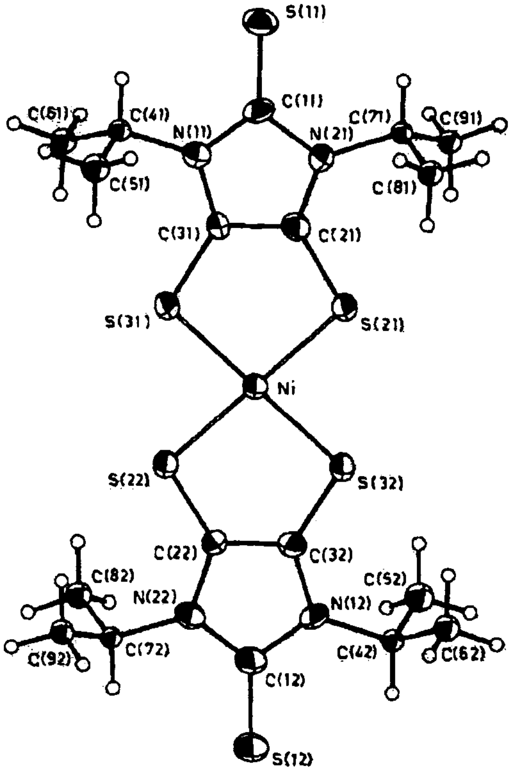


FIGURE 2.2 Molecular structure of 7 and the corresponding atom-labelling scheme. Selected bond lengths (Å): Ni-S(21) 2.161(4), Ni-S(31) 2.158(4), Ni-S(22) 2.159(4), Ni-S(32) 2.156(4), S(11)-C(11) 1.65(1), S(21)-C(21) 1.70(1), S(31)-C(31) 1.70(1), S(12)-C(12) 1.65(1), S(22)-C(22) 1.69(1), S(32)-C(32) 1.69(1), N-$C_{ring}$ range from 1.35(2) to 1.40(2), $C_{ring}$-$C_{ring}$ range from 1.38(1) to 1.39(1)

X-ray structural data of 7 (**Figure 2.2**) confirm that the metal atom lies in a square-planar coordination involving two vicinal sulfur atoms from each of two independent chelating molecules and that molecule results roughly planar if the S atom and the $Pr^i$ groups are excluded. The $Pr^i$ groups are perpendicular to the imidazoline rings and prevent the formation of stacks with short intermolecular contacts. This is consistent with the insulating behaviour of this compound while the structurally analog [Ni(dmit)$_2$], which shows interstack S···S contacts, is a semiconductor.[10b]

The cyclic voltammogram of 7 in $CH_2Cl_2$ is reported in **Figure 2.3**. Two reversible one-electron reductions ($E^1_{1/2} = -0.13$ V and $E^2_{1/2} = -0.60$ V) and a *quasi*-reversible oxidation ($E_{an} = +0.78$ V) are observed.

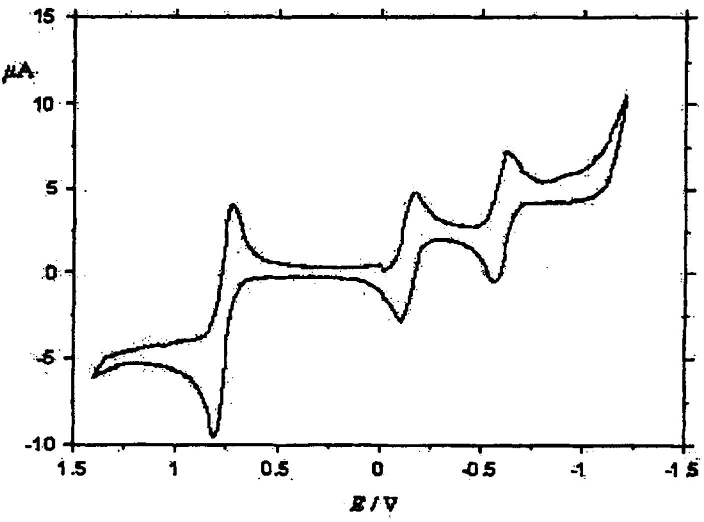


FIGURE 2.3 Cyclic voltammogram of 7: solvent, $CH_2Cl_2$; supporting electrolyte, $Bu_4NPF_6$ (0.1 mol dm$^{-3}$); temperature, 298 K; reference electrode, Ag/AgCl/KCl saturated; working electrode, Pt wire; internal standard, $F_c^+/F_c$ ($E_{1/2}$=0.48V); scan rate, 100 mV s$^{-1}$

Both reductions for $E^1_{1/2}$ and $E^2_{1/2}$, ascribed to the processes giving rise to the monoanion and dianion of 7, are shifted to more negative values than those of [Ni(dmit)$_2$]$^-$ ($E^1_{1/2} = 0.22$ V and $E^2_{1/2} = -0.13$V[21]) while, with respect to other nickel-dithiolenes, including the unsubstituted 1,2-dithiolene complexes, $E^1_{1/2}$ is shifted to more negative values and $E^2_{1/2}$ to more positive ones.[8] The shift in the positions of the redox potentials is reflected in the stability of the neutral complex, directly isolated, whereas the neutral $[Ni(dmit)_2]$ species has only been isolated by the electrochemical oxidation of the anion $[Ni(dmit)_2]^-$.[22]

In accordance with electrochemical data, the chemical reduction of **7** with 1,2- or 1,4-phenylendiamine produces the monoreduced species $Bu_4N[Ni(Pr^i_2timdt)_2]$ (**8**).

The electronic spectrum of **8** in the near-IR region is reported in **Figure 2.4**. The observed strong band is still assigned to the transition $b_{1u} \rightarrow b_{2g}$ which remains possible being the $b_{2g}$ orbital singly occupied in the anion. This transition is found at $\lambda = 1384$ nm ($\varepsilon \sim 30000$ dm$^3$ mol$^{-1}$cm$^{-1}$) in $CH_3CN$ and undergoes a shift to higher wavelength ($\lambda = 1402$ nm) in $CHCl_3$ solution. X-ray structural studies reveal that **8** consists of discrete $[Ni(Pr^i_2timdt)_2]^-$ anions and $Bu_4N^+$ cations. In the anion the metal atom is coordinated by two vicinal sulfur atoms of two independent ligands in a square-planar geometry with slight tetrahedral deformation.

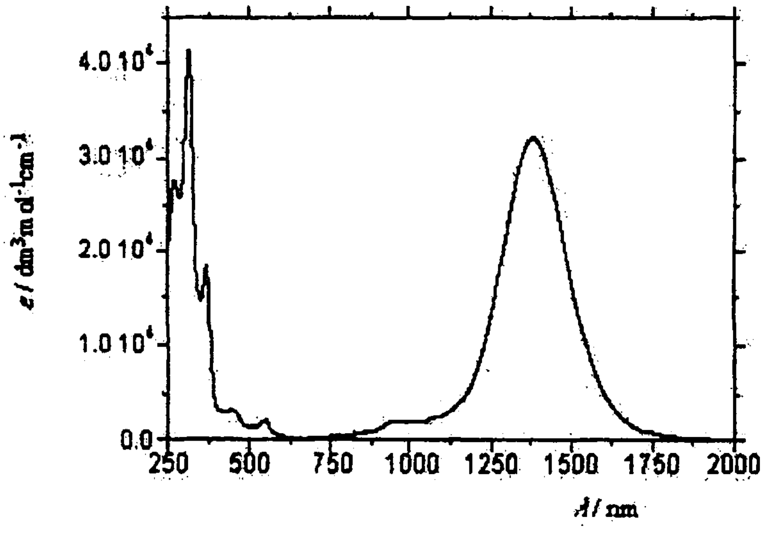
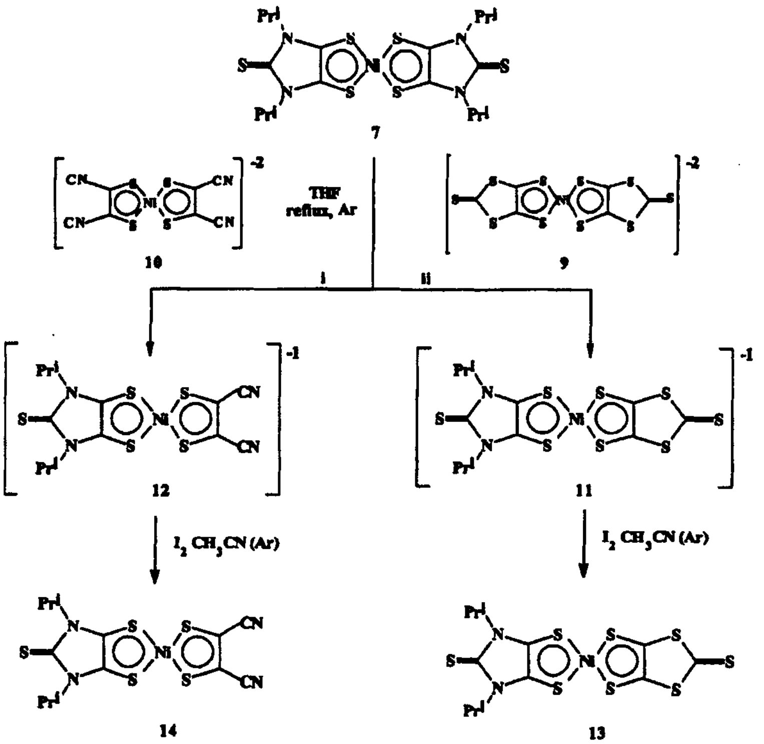


FIGURE 2.4 UV-VIS-NIR spectrum of **8** in $CH_3CN$ solution

## 3. UNSYMMETRICAL NICKEL-DITHIOLENES

With the goal of further tuning the NIR-absorption by a combination of different ligands, unsymmetrical (or mixed-ligand) nickel-dithiolenes bearing $Pr^i{}_2$timdt and dmit or mnt, have been prepared[11] (see Scheme 3.1).



SCHEME 3.1 i=3 days for 80% conversion of 7 ($c=1.81*10^{-3}$ moldm$^{-3}$); ii=5 hours for desappearance of 7 ($c=6.17*10^{-3}$mol dm$^{-3}$)

Well documented examples of unsymmetrical Ni-dithiolenes are rare,[23] mainly for the difficulties encountered in the purification of the products, often contaminated by the symmetrical precursors. **11** and **12** are formed through a slow reaction which seems to reach completeness asintotically. Indeed, no backward reaction is observed upon dilution and upon lowering the temperature. While **11** is formed through the corresponding symmetrical monoanionic dithiolenes, produced as reaction intermediates, no symmetrical monoanionic intermediates are observed in the formation of **12**. This can be observed following the course of the reactions spectrophotometrically. Side undesired reactions are observed when the reagents are left without protection from air and/ or moisture.[24]

The mixed-ligand complexes **11** and **12** show in $CH_3CN$ strong absorptions at $\lambda = 1194$ ($\varepsilon = 22800$ $dm^3$ $mol^{-1}$ $cm^{-1}$) and 1070 nm ($\varepsilon = 19400$ $dm^3$ $mol^{-1}$ $cm^{-1}$) respectively. In Figure 3.1 the spectra of **11**, **12** and $[Bu_4N][Ni(Pr^i_2timdt)_2]$ **8** (in $CH_3CN$; $\lambda = 1384$ nm, $\varepsilon = 32100$ $dm^3$ $mol^{-1}$ $cm^{-1}$) are reported. The observed Near-IR absorptions are in accordance with the expectations as previously cited since the dmit and mnt ligands exhibit increasing electron-withdrawing power.

TABLE III.1 Electrochemical data for the unsymmetrical and symmetrical-related complexes, $E_a$ = anodic potential; $E_{1/2}$= half- wave potential

| *Complex* | $E_a$ *(V)* ($ML_2^- \rightarrow ML_2^0 + e^-$) | $E_{1/2}$ *(V)*[a] ($ML_2^- + e^- \rightleftarrows ML_2^{2-}$) |
|---|---|---|
| **11** | +0.234[b] | −0.402 |
| **12** | +0.386[c] | −0.307 |
| **7** | −0.100[c] | −0.598 |
| **9** | +0.316[b] | −0.109 |
| **10** | +1.110[b] | +0.270 |

a. Measured using a Pt wire working electrode, Pt wire as counter electrode, Ag/AgCl (KCl saturated) as reference electrode at a 100mV/s scan rate, $CH_3CN$ as solvent containing 0.1 mol $dm^{-3}$ $Bu_4NPF_6$ electrolyte. Half-wave potential for ferrocene/ferrocenium couple (internal standard) is 0.43 V at the above conditions. Temperature 25°C.

b. Irreversible.

c. Reversible one-electron oxidation: $E_{1/2}$(**12**) (**7**) = +0.354; $E_{1/2}$ = − 0.134 V.

Electrochemical data of **11** and **12**, together with those of the related samples are shown in Table III.1. One reversible mono-electronic reduction wave for both complexes and one oxidation wave irreversible for **11** and reversible for **12** are observed in the cyclic voltammograms. The $E_{1/2}$ values are intermediate between those of the corresponding parent

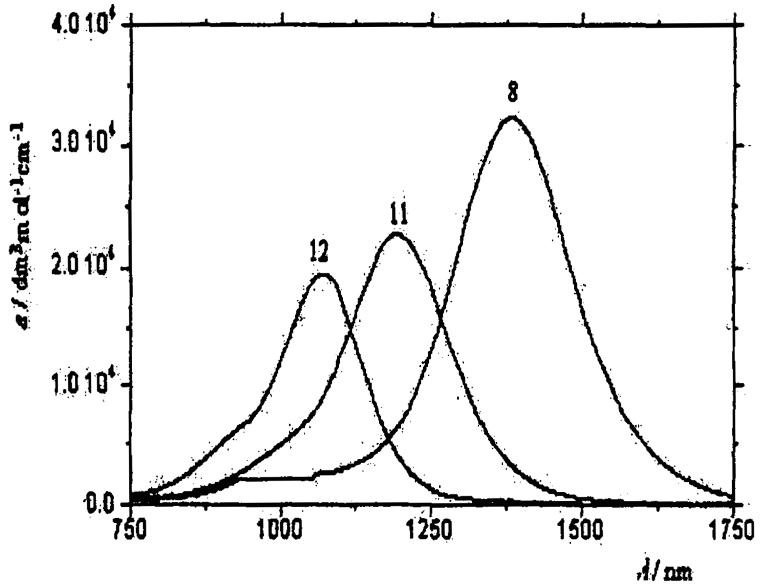


FIGURE 3.1 Comparison of the spectra in $CH_3CN$ of $[Bu_4N][Ni(Pr^i_2timdt)(mnt)]$ **12**, $[Bu_4N][Ni(Pr^i_2timdt)(dmit)]$ **11** and $[Bu_4N][Ni(Pr^i_2timdt)_2]$ **8** in the NIR region

complexes, showing that also the electrochemical properties of these unsymmetrical dithiolenes can be tuned by a combination of ligands.

The neutral $[Ni(Pr^i_2timdt)(dmit)]$ (**13**) and $[Ni(Pr^i_2timdt)(mnt)]$ (**14**) complexes have been prepared by chemical oxidation of **11** and **12** with $I_2$. A significant shift to higher frequencies is observed upon oxidation and a comparison of the spectra of **12** and **14** is reported in **Figure 3.2.** The comparison of the spectra of **11** and **13** in the same solvent could not be made due to solubility reasons. Spectra of **13** have been monitored in $CS_2$ only ($\lambda = 1056$ nm). The poor solubility of **13** is related to its structural features. **13** has been structurally characterized.[11] Chains along *b* are formed through contacts between the terminal sulfur atoms of the $Pr^i_2$timdt and dmit ligands [S···S= 3.243(2)Å]. The C=C distances, which should be most significant for determining the charge of the ligands, are shorter in the dmit fragment than those in

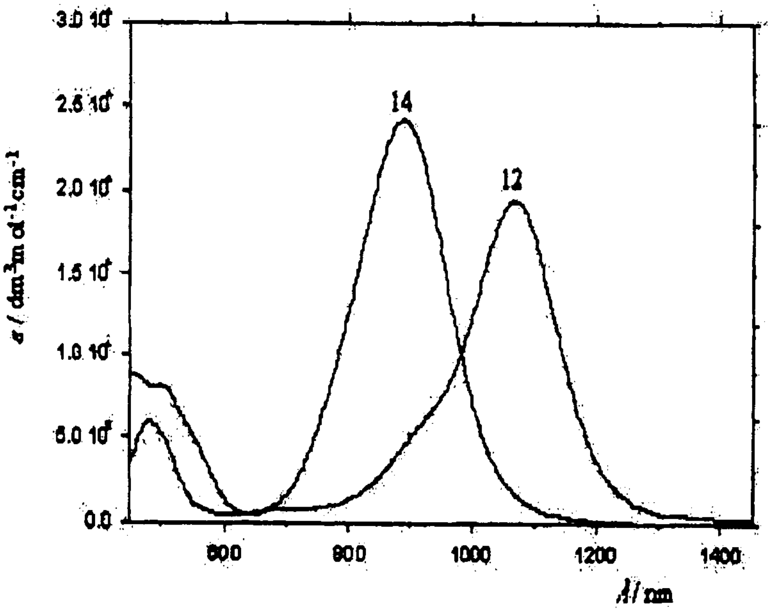


FIGURE 3.2 Comparison of the spectra in $CH_3CN$ of $[Bu_4N][Ni(Pr^i{}_2timdt)(mnt)]$ **12** and $[Ni(Pr^i{}_2timdt)(mnt)]$ **14** in the NIR region

$[Bu_4N][Ni(dmit)_2]$ and similar in $Pr^i{}_2timdt$ to those found in $[Ni(Pr^i{}_2timdt)_2]$. The latter complex being neutral structural data may suggest that the negative charge is more localised in the dmit ligand than in the $Pr^i{}_2timdt$ one. Raman scattering has been shown to be suitable to correlate the C=C frequency and the charge for the $[M(dmit)_2]^{n-}$ ($n = 0$, 0.29, 0.5, 1, 2; M =Ni, Pd) case.[25] Raman peaks which can be assigned to the C=C stretching vibration for the $[Ni(Pr^i{}_2timdt)(dmit)]^{n-}$ compounds ($n = 0$, 1388 $cm^{-1}$; $n = 1$, 1396 $cm^{-1}$) have been observed and reported in this correlation (**Figure 3.3**). The position of these bands, very close to the frequency of the C=C peak for $[Ni(dmit)_2]^{-1}$, seems to be in accordance with structural results which suggest that dmit ligand in the neutral mixed-ligand complex bears more negative charge than $Pr^i{}_2timdt$. Similarly $[Ni(Pr^i{}_2timdt)(mnt)]$ shows a strong peak at 1425 $cm^{-1}$ very near to the frequency of the C=C peak for $[Ni(mnt)_2]^{-1}$ in accordance with a higher content of the negative charge on the mnt ligand.[26] This different distribution of the charge may be taken into account by considering that the composition of the HOMO and the LUMO, described as π-orbitals delocalised over both ligands in the neutral symmetrical complexes, will be modified in the mixed-ligand complexes. Orbitals residing at lower energy (mnt and dmit) will contribute more to the HOMO, while orbitals residing at higher energy ($\mathrm{Pr}^i{}_2$timdt is more electro-donating ligand) will contribute more to the LUMO. Since the C=C bond components in this orbital are bonding,[27] the population of this orbital will produce an accumulation of negative charge on the electro-donating ligand. Theoretical calculations are required to confirm this conclusion. Nevertheless, the whole experimental results seem to suggest that these mixed-ligand complexes are still describable as (delocalized) dithiolene rather than dithiolate-dithione derivatives.

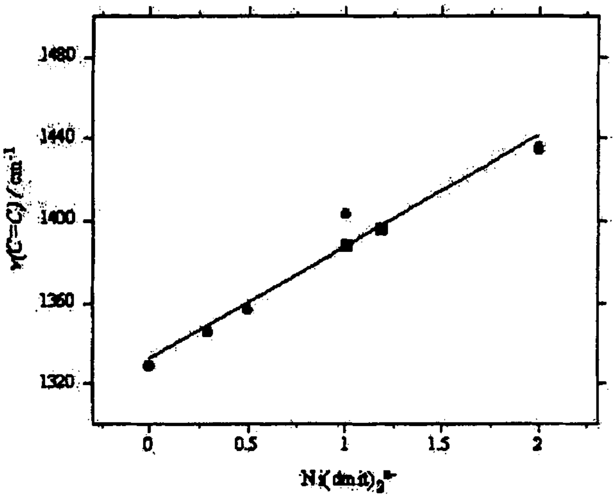
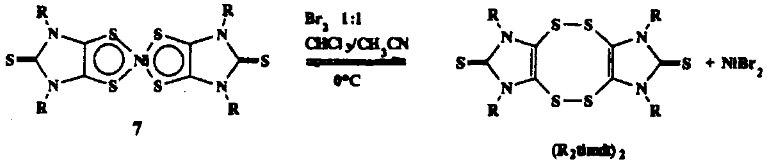


FIGURE 3.3 The C=C vibration *versus* the charge ($n^-$) of dmit-based nickel complexes (•), showing a linear correlation.[25] Raman shifts of 11 and 13 are enclosed (■)

## 4. [Ni($R_2$timdt)$_2$] AS PRECURSORS OF SULFUR RICH DONORS

In this section the attention is devoted to describing new aspects of the chemistry of [Ni($R_2$timdt)$_2$], where the latter compounds serve as precursors in the synthesis of sulfur-rich electron donor molecules of interest in coordination chemistry, in the field of charge-transfer adducts and of anticancer agents. As described in Section 2, the synthesis of **7** was achieved by the *in situ* sulfurization of 1,3-dialkylimidazolidine-2-thione-4,5-dione in the presence of Ni powder. In the absence of the metal the obtained product was generally **5**, which is unsuitable to be used as a source of $R_2$timdt. A convenient source of $R_2$timdt is instead obtained by reacting **7** with equimolar amount of $Br_2$, according to the scheme reported below:



The obtained product revealed to be ($R_2$timdt)$_2$ consisting of $R_2$timdt units connected by disulfide linkers, which can be easily broken. Thus through the above reaction, a highly suitable source of $R_2$timdt dithiolene ligands, which can be stored being a well-defined and stable precursor for metal-dithiolenes, is derived. This is especially relevant when the *in situ* sulfurization preparative method does not work since the other reagents present in the reaction mixture (Lawesson's reagent and its derivatives after sulfurization) can compete with the dithiolene ligand for the metal.

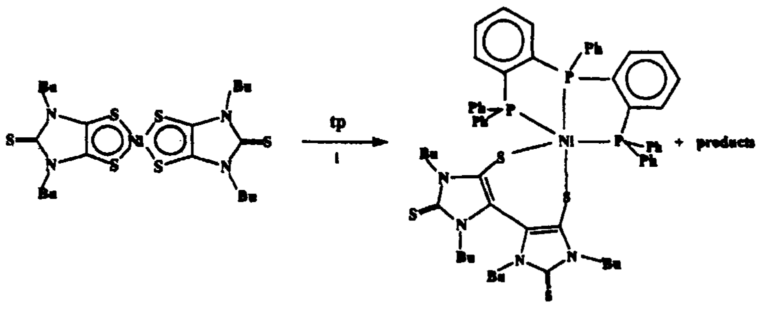
It must be remarked that the synthesis of ($R_2$timdt)$_2$ was not achieved by standard methods except for the case where R= $\mathrm{Pr}^i$ but in trace amounts.

The corresponding reactions with IBr and $I_2$, dihalogens with increasing acceptor- and decreasing oxidation-power have been performed. The potential capability of the ligand to work as a donor, even though in its dimeric form or coordinated to a metal, is due to the presence of the thionic-sulfur donor in the periphery of the molecule. The addition of increasing amount of IBr in $CH_3CN$ to **7** in $CHCl_3$ (molar ratios **7**:IBr

=1:4) produces an orange crystalline solid formulated as $(\mathrm{Pr}^{i}_{2}\mathrm{timdt})_2\cdot\mathrm{I}_{2.5}\,\mathrm{Br}_{1.5}$, on the basis of analytical and spectroscopic results. When working with a very large IBr excess with respect to **7** (1:60 molar ratio between the reagents) a salt consisting of a dication $[\mathrm{C}_{18}\mathrm{H}_{28}\mathrm{I}_2\mathrm{N}_4\mathrm{S}_4]^{2+}$, containing two 2-iodo-1,3-dialkylimidazolium groups linked through two disulfide bridges, and $\mathrm{IBr}_2^-$ as counterions (**15**) has been obtained.[12] The comparison of the structural features of **15** with similar compounds where shorter cation-anion distances were observed, and explained in therms of a covalent interaction between the C-I group ($\sigma$-acceptor) of the 2-iodo-imidazolium cation towards $\sigma$-donors (carbene, $\mathrm{I}^-$, $\mathrm{I}_3^-$...) shows that instead the potential $\sigma$-donor $\mathrm{IBr}_2^-$ interacts with the cation mainly with an interaction of an ionic type.

By reacting $\mathrm{I}_2$ with **7** depending on the molar ratios of the reagents both neutral adducts (where two $\mathrm{I}_2$ molecules interact with each peripheral sulphur atom of the ligand) and $[\mathrm{Ni}(\mathrm{Pr}^{i}_{2}\mathrm{timdt})_2]\cdot\mathrm{I}_6$, consisting of a dinuclear compound in which the ligand occurs in different oxidation states have been obtained. This latter compound is formed by the neutral adduct $[\mathrm{Ni}(\mathrm{Pr}^{i}_{2}\mathrm{timdt})_2]\cdot 2\mathrm{I}_2$ and by a complex $[\mathrm{Ni}(\mathrm{I}_2)(\mathrm{Pr}^{i}_{2}\mathrm{timdt})_2]$, where the nickel(II) is octahedrically coordinated with two iodides at apices and two chelating ligands (formally in the neutral form). The adduct and the octahedral complex are connected through diiodine molecules in such a way that a sequence of twelve iodine atoms $\mathrm{S}\cdot\mathrm{I}_2\cdots\mathrm{I}_2\cdots\mathrm{I}^-\cdots\mathrm{I}_2\cdots\mathrm{I}^-\cdots\mathrm{I}_2\cdots\mathrm{I}_2\cdot\mathrm{S}$ is formed.[10b] A novel ligand 5,5′-bis(1,3-dialkyl-4-imidazoline-2-thione-4-thiolate] ($\mathrm{R}_4$btimdt) whose coordination chemistry is under investigation, has been unexpectedly obtained by reacting **7** with a tri-functional phosphine [tp=bis(2-diphenylphosphinophenyl)phenylphosphine] while with mono- ($\mathrm{PPh}_3$) or bi-functional [dppe=1,2-bis(diphenylphosphino)ethane] phosphines the reagents are recovered unchanged.[13] The reaction product [Ni(tp)($\mathrm{R}_4$btimdt)] (R=Bu, **16**) was obtained according to Scheme 4.1.

**16** has been structurally characterized. Complex **16** contains the first example of the S,S dinegative chelating ligand $\mathrm{Bu}_4$btimdt, generated *in situ* by elimination of one of the two vicinal sulfur atoms on each ligand coordinated to the metal in the nickel dithiolene with concomitant C-C coupling between the two imidazole rings. The driving-force for the formation of the observed complex **16** should be related to two favourable factors: the stability of the pentacoordinated $\mathrm{Ni}^{\mathrm{II}}$ complexes with tripo-

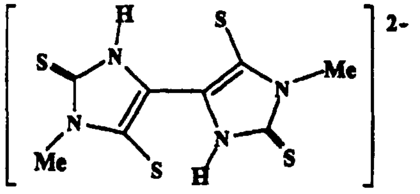


7 16

SCHEME 4.1 i = tp excess, THF, reflux under $N_2$, 24 h

dal P-ligands, coupled with the capability of the ligands in **7** to give rise to C-C coupling between the imidazoline rings as observed when trying to prepare the neutral precursors of the ligand in **7** by sulfurization of **4**. No C-C coupling between the rings is observed when using dmit-based nickel-dithiolenes, showing once more the peculiarity of chemical behaviour of the $[Ni(R_2timdt)_2]$ class among nickel-dithiolene complexes.

A dianion, $H_2X^{2-}$, belonging to the same class of $R_4btimdt^{2-}$ has been previously obtained *via* an unusual method by reacting elemental sulfur with 1-methylimidazole.[17]



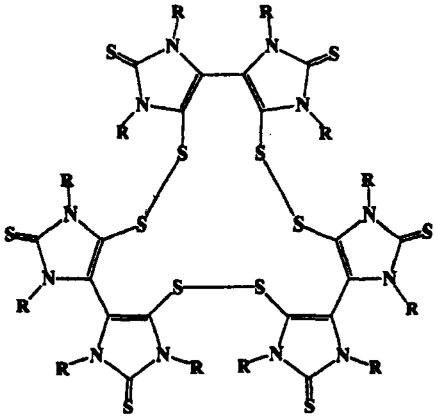
$H_2X^{2-}$

This anion was isolated in the solid state as the $(PPh_4)_2H_2X$ salt, structurally characterized and proposed as a new ligand of special interest owing to its multi-electron redox properties.

However, to the best of our knowledge, its coordination chemistry is still unexplored. Also a neutral compound obtained for oxidation of this ligand has been isolated but not characterized. The $R_4$btimdt anions are clearly related to the class of **5**. This class of molecules exhibit promising anticancer properties[28] now under testing *in vivo* by National Cancer Institute of Bethesda (USA). By reacting **5** with an alcoholate, the $R_4$btimdt anion is formed in solution and can be isolated in the complex [Ni(dppe)($R_4$btimdt)], when [Ni(dppe)$Cl_2$] is added to the reaction mixture, buffered with ammonium acetate.

When non-coordinated, the anion is oxygen sensitive and the attempts to isolate it as a salt gave a mixture from which the new macrocycle **17** was isolated in low yield (see below). Macrocycle **17** is prepared more conveniently (40% yield) by buffering with ammonium acetate and oxidizing the reaction mixture with $O_2$ or $H_2O_2$.[13] **17** can be considered as a trimer of $R_4$btimdt where the monomeric units are linked together through disulfide bridges.

The structural data are similar to those previously observed by us in thione derivatives with similar moieties.[14,29,30]



**17**

In conclusion a novel desulfurization reaction with concomitant C-C coupling between two imidazoline rings, never reported previously, has been found. This reaction represents a promising template synthesis to prepare, starting from nickel-dithiolenes, new chelating S,S-dianionic ligands, which are not easily attained by other routes.

The donor properties of **5** towards acceptors such as dihalogens[29] and metals[30] have been previously investigated. The reaction with diiodine produces CT complexes. The reactions of **5**, **6** and **17** towards similar and other acceptors such as fullerenes with the view to obtain CT adducts are under investigation. The presence of the sulfur atoms and their structural features make these donors suitable to prepare CT adducts with $C_{60}$. In fact the presence of flexible sulfur linkers between eterocycles in similar donors has been shown to be a favourable factor to allow a change in the conformation of the donors adapting it to the spherical rigid form of $C_{60}$.[31,32]

## 5. CONCLUSIONS

New near-IR dyes working in the 880–1400 nm range based on symmetrical and unsymmetrical nickel-dithiolene complexes bearing $R_2$timdt have been described. In the $R_2$timdt ligand, the presence of N-electron donor atoms of the imidazoline ring forced into co-planarity with the dithiolene ring, revealed to be valuable to shift the low energy transition typical of this class of complexes in a region of remarkable interest for near-IR dyes, while stability was maintained. The symmetrical neutral complexes absorb very strongly at approximately 1000 nm, region of special interest for NIR-dyes in order to be used in Q-switching Neodymium lasers, which operate at 1064 nm. Moreover these complexes work as switchable near-infrared dyes, since the absorption is shifted to approximately 1400 nm on reversible reduction. The high thermal and photochemical stability of the complexes at the laser wavelength add value to these new NIR-dyes for practical applications. In the unsymmetrical nickel-dithiolene complexes involving both the $Pr^i{}_2$timdt and dmit or mnt ligands a tuning of the NIR-absorption depending on the combination of the ligands and of the charge is achieved.

The potential of $[Ni(R_2timdt)_2]$ to work as precursors of sulfur-rich donors which are not easily to obtain by conventional routes has also been shown, and several new molecules of interest in coordination chemistry, in the field of charge-transfer adducts and of anticancer agents have been obtained.

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