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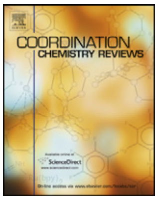

Review

# Square-planar $d^8$ metal mixed-ligand dithiolene complexes as second order nonlinear optical chromophores: Structure/property relationship

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### Contents

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ABSTRACT

The structure/property relationship of square-planar $d^8$ metal *push*/*pull* mixed-ligand dithiolene complexes is discussed to provide suitable tools to chemists for tailoring compounds with predictable optical properties. These complexes exhibit a typical HOMO–LUMO electronic transition which falls at low energies (vis–NIR region). Substituents at the dithiolene core affect the energy of the frontier orbitals and mixed-ligand complexes based on two different ligands give rise to an asymmetric-symmetric distribution of the charge according to the differences in the *push*/*pull* character of the two ligands. Where the *push*/*pull* character of the two ligands is significantly different, a $\pi$ localized electron distribution occurs. The *pull* ligand (dithiolate) contributes mostly to the HOMO, the *push* ligand (dithione) mostly to the LUMO, and the HOMO–LUMO transition has ligand-to-ligand charge-transfer (CT) character with some contribution of the metal. These chromophores exhibit negative solvatochromism and molecular first hyperpolarizability.

Where the difference in the *push*/*pull* character of the two ligands is small, a $\pi$ delocalized electron distribution occurs and the chromophores exhibit optical features typical of symmetrical complexes (NIR dyes, no second order NLO activity).

Structural data, spectroscopic and electrochemical features reflect the $\pi$-delocalized/localized electron distribution, and suitable markers such as $\lambda_{max}$, $\varepsilon$; $\nu$(C=C); reduction potentials work well to distinguish the limiting forms and to predict optical properties.

Analogies in the optical features exhibited by $d^8$ metal diimino–dithiolate complexes are highlighted.

## 1. Introduction

### 1.1. Background

Metal-dithiolene complexes are object of extensive studies since their initial synthesis to current years both for their intrinsic interest and for their applications as molecular materials with

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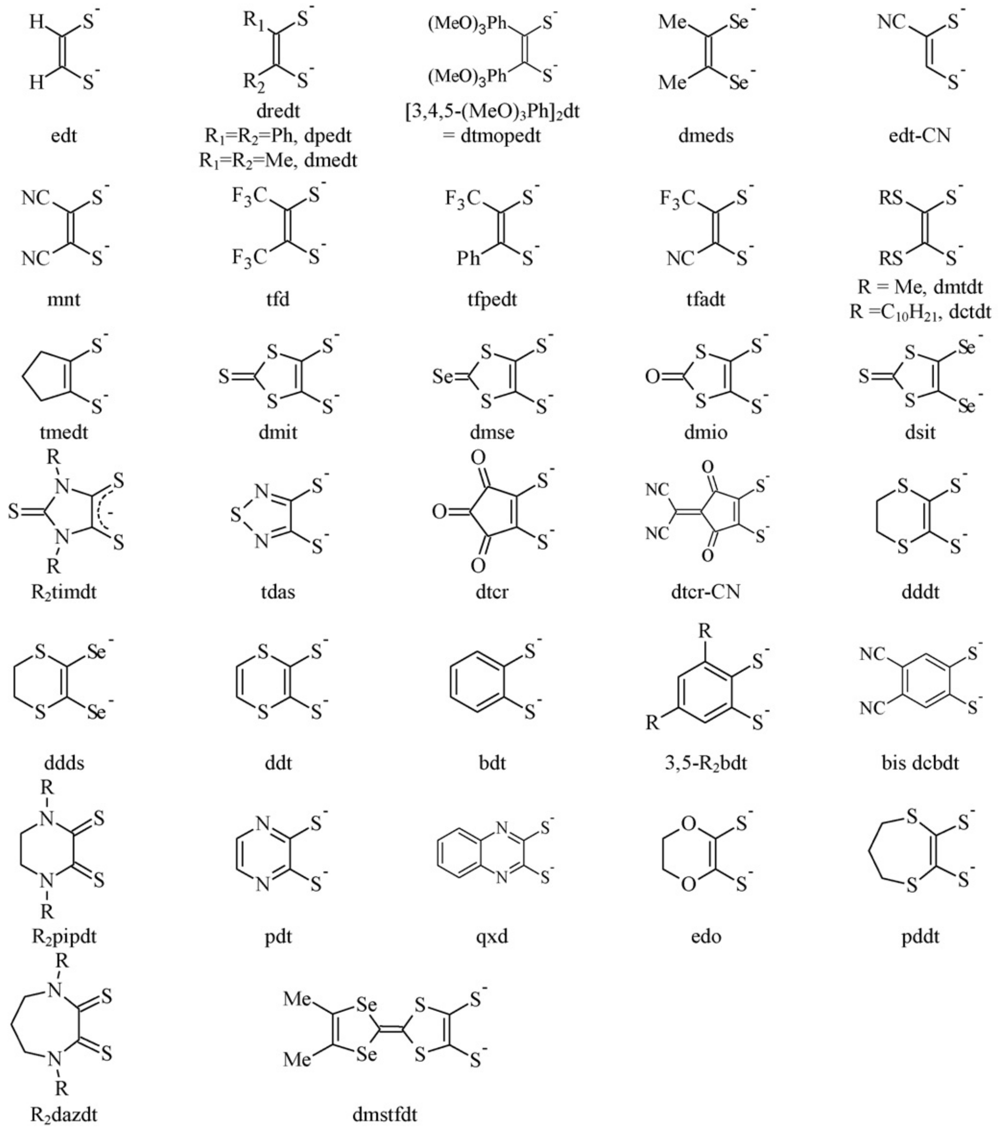
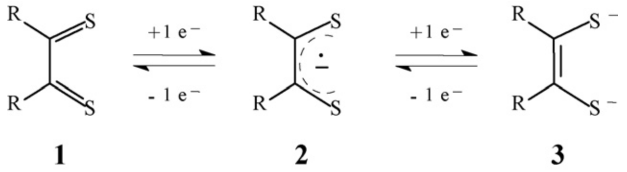


**Chart 1.**

conducting [1], magnetic [2] and optical [3,4] properties, as well as their involvement in bioinorganic processes at the catalytic centers of Mo and W oxotransferases [5]. In particular square-planar $d^8$ metal complexes have been investigated for their relevant optical properties [3,4], and can be useful as near infrared dyes for Q-switching the Nd:YAG lasers as shown by the Mueller–Westerhoff pioneering work [6]. Optical properties, in particular nonlinear properties are of interest for a number of photonic applications, including high speed optical switching, telecommunication, optical data processing and storage [7]. Nonlinear optical properties arise when the interaction of radiation with the matter, which at small field induces an instantaneous displacement (polarization: $P_0 = \mu = \alpha E$ where $\alpha$ is the linear polarizability) of the electronic density away from the nucleus (linear optics), involves high fields (laser light). In this last case the polarizability of the molecule can be driven beyond the linear regime and a nonlinear polarization is induced (NLO): $P_m = \alpha E + \beta E^2 + \gamma E^3 + \cdots$ and for the bulk material $P = P_0 + \chi_1 E^2 + \chi_2 E^3 + \cdots$ where $\beta$ and $\gamma$ are the molecular first and second order hyperpolarizabilities ($\alpha \gg \beta > \gamma > \cdots$) and $\chi_1$ and $\chi_2$ are the first and second order NLO susceptibilities (second and third order effects, respectively). Most often molecules with extensive π delocalized system are required to promote NLO properties. Among these, symmetric and asymmetric square-planar $d^8$ metal–dithiolene complexes can be suitable to generate third order NLO properties [8], but only asymmetric complexes at the molecular level, such as mixed-ligand complexes with *push*/*pull* ligands, and a non-centrosymmetric crystal packing for a bulk material, are required to generate second order NLO properties [4b,7,9]. No simple guidelines to design complexes to generate third order NLO are available, while a satisfactory structure–property relationship for second order NLO chromophores has been provided. Accordingly this review is addressed to focus on the potential of the class of square-planar $d^8$ metal mixed-ligand complexes in generating second order NLO properties; to compare the nature of the bonding in these and in $d^8$ metal diimine–dithiolato complexes, another class of mixed-ligand dithiolene compounds; and to provide a structure/property relationship which can be useful for tailoring suitable complexes to generate the desired properties. Reviewing other relevant properties of square-planar $d^8$ metal mixed-ligand complexes, such as third order NLO properties [8], or their use as component of multifunctional molecular materials with optical and/or magnetic and conducting properties [1a,10] is out of the scope of the present review.



**Scheme 1.**

### 1.2. Dithiolene ligands and $d^8$ metal bis-dithiolene complexes

The dithiolene ligands considered in this review are depicted in Chart 1.

Dithiolene are redox-active ligands (see Scheme 1), capable to coordinate a variety of metals as neutral dithioketones, (**1**), as ene-1,2-dithiolate dianions (**3**), as mixed-valence thioketone-radical thiolate monoanions (**2**). The term dithiolene is used independently of the formal oxidation state of ligands to reflect their noninnocent character in several metal complexes [11].

According the Jørgensen definition, “ligands are innocent when they allow oxidation states of the central atoms to be defined” [12]. More recently Ward and McCleverty [13] have pointed out that the term noninnocent is applied properly when it is referred to a particular combination of the metal and the ligand rather than to redox-active ligands alone. When, metal-centered and ligand-centered orbitals lie at different energies, their redox potentials are well separated and the related redox processes can be assigned to the metal or the ligand without ambiguity; on the contrary, ambiguity is found where a significant mixing between the metal-centered and ligand-centered orbitals occurs. Thus the same ligand can behave as innocent or noninnocent depending on the metal involved in the complexes.

In the class of square-planar $d^8$ metal–dithiolenes, the members of the series which may spread from the dianionic to the dicationic form [14] can be connected through reversible one-electron redox steps as shown in Eq. (1).

$$[M(S_2C_2R_2)_2]^{2+} \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} [M(S_2C_2R_2)_2]^{+} \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} [M(S_2C_2R_2)_2]^{2+} \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}}$$

$$\times [M(S_2C_2R_2)_2]^{-} \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} [M(S_2C_2R_2)_2]^{2-} \qquad (1)$$

The 2+ and 2− limits in the members of the series are due to the fairly isolated frontier π-MOs, shown in Fig. 1, which can be either empty or populated. These MOs are the *in phase* (*i.p.*) and *out-of phase* (*o.o.p.*) combinations of a $C_2S_2$ orbital, and are at high energy due to the C–S and S···S antibonding interactions within one ligand and between the two ligands [15]. These orbitals are stabilized and destabilized by one high lying $p_\pi$ and a lower $d_\pi$ metal orbital, respectively. The d-metal orbitals stabilized relative to ligand orbitals lead to an “Inverted Bonding Scheme” [16], while in a “Normal Bonding Scheme” the d-orbitals are destabilized relative to the ligand orbitals. The entity of mixing between the metal-centered and ligand-centered orbitals provides the “non-innocent/innocent” character to the ligands.

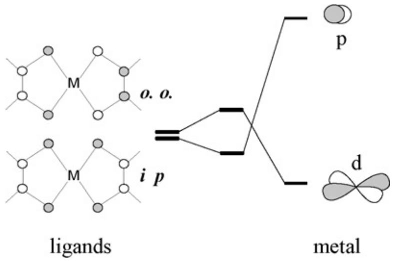


**Fig. 1.** Frontier MOs in square-planar $d^8$ metal-dithiolene complexes formed by the *in phase* (*i.p.*) and *out-of-phase* (*o.o.p.*) combinations of $C_2S_2$ orbitals perturbed by the metal.

The electronic effects on the frontier orbitals of various substituents at the dithiolene core have been quantified [15–17]: in general, $C_2S_2$ π donor substituents (*push*) raise the energy of the HOMO and the LUMO, whose gap is lowered by a lowered interaction of the ligands orbitals with the low lying metal orbitals. Whether the HOMO is pushed up at too high energy, an induced increased reactivity leads to the loss of one ($[M(II)L_2]^+$) or two electrons ($M(II)L_2]^{2+}$) so that also this orbital is preferentially depopulated. In contrast, π acceptor substituents (*pull*) lower the energy of both the MOs and favour the dianionic state.

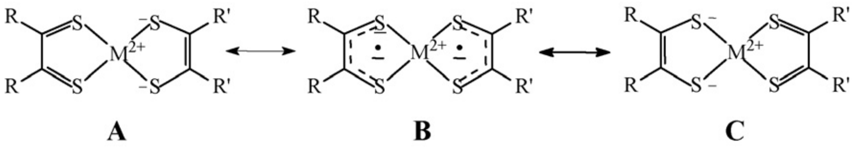
Following the Lewis formalism to summarize the bonding in these systems, classical structures involving the metal in the 2+ oxidation state and the ligands in the 1,2-dithione and 1,2-ene-dithiolate form respectively can be applied only to the diamagnetic dicationic and dianionic members of the series. For the neutral diamagnetic complex two bonding descriptions are required: one involves a resonance hybrid among the limiting forms where the M(II) is coordinated to one neutral dithione molecule and one dithiolate dianion (see forms **A** and **C** in Scheme 2). The other non-classical Lewis description involves the M(II) coordinated to two ligands in radical form where the spins are antiferromagnetically coupled [18].

Similarly, nonclassical Lewis descriptions are required to describe the monocationic and monoanionic complexes where the M(II) is coordinated respectively to one dithione ligand and one ligand in radical form, and to one dithiolato ligand and one ligand in radical form with the spin ($S = 1/2$) highly delocalized over the molecule.

In neutral symmetric complexes ($R = R'$ in Scheme 2), the overall π-electron delocalization (form **B**) implies the equivalence of resonance structures **A** and **C**. As stated above only the low lying orbital is populated and the HOMO–LUMO dipole allowed transition ($b_{1u} \rightarrow b_{2g}$) gives rise to the typical intense electronic transition which falls at low energies (near infrared region, NIR) [17]. Complexes absorbing at approximately 1000 nm, are dyes suitable for Q-switching neodymium lasers. High thermal and photochemical stability of the dye at the laser wavelength in addition to high absorptivity of the NIR transition is required for practical use [17a]. In the monoanionic paramagnetic derivative the LUMO becomes the half-filled SOMO and the related HOMO–SOMO transition undergoes a bathochromic shift and a decrease in intensity, while in the dianionic derivatives a bleaching is observed because the former LUMO becomes doubly occupied. The distinct NIR absorption spectra of the redox-active members of the series make these complexes polyelectrochromic NIR dyes.

In neutral asymmetric complexes, different terminal groups attached to the dithiolene core ($R \neq R'$) may cause a redistribution of the π electrons. Where the differences in the *push*/*pull* character of the two ligands are small, mixed-ligand complexes show ground state describable with the limiting form **B** (π-delocalized systems) and optical features typical of symmetrical complexes (NIR dyes, no second order NLO activity) are predictable [19].

Where one ligand coordinates as neutral dithione and the other as dithiolato dianion a redistribution of the π electrons toward one of the limiting π localized forms, **A** or **C** occurs [15]. In this case the *pull* ligand gives a prevailing contribution to the HOMO, and the *push* one to the LUMO. The characteristic absorption band which undergoes solvatochromic shift can be assigned to a charge-transfer (CT) HOMO–LUMO transition having inter-ligand, with some metal mixing, character. Due to these features mixed-ligand bis-dithiolene complexes are potential second order chromophores, and most often they exhibit molecular first hyper-



**Scheme 2.**

polarizability ($\beta$), as shown in some nickel cases reported by us [20] and others [21].

### 1.3. $d^8$ metal diimine–dithiolato complexes

These complexes show a variety of properties such as photoluminescence in solution [22], negative solvatochromism [22a], redox activity [23] and large excited state potentials [24] which are studied for possible applications in dye-sensitized solar cells [25] and recently for the photogeneration of $H_2$ from $H_2O$ using an integrated system based on $TiO_2$ and their Pt-derivatives [26]. For details on these relevant aspects readers are referred to the cited papers.

As far as the nature of the bonding is concerned, these compounds, similarly to mixed-ligand dithione–dithiolato complexes, bear two different unsaturated chelating ligands, one more easily reduced (acceptor, in this case diimine instead of dithione), the other more easily oxidized (donor, dithiolato) [27].

A resonance hybrid among the limiting forms depicted in Scheme 3 can be taken into account to describe the bonding following the Lewis formalism analogously to what shown in Scheme 2 for neutral asymmetrical dithiolenes.

When the resonance form **A** is prevailing, a π-localized system describes the ground state, while the equivalence of resonance structures **A** and **C** implies the overall π-electron delocalization (form **B**). Most of the investigated complexes are describable as π-localized system and are characterized by an absorption in the visible region with medium to low molar absorption coefficients (in the 6000–13,000 $M^{-1}\,cm^{-1}$ range) and a large negative solvatochromism [22a,27]. Based on theoretical and experimental studies [22a,24,27], CT character has been assigned to this peak which is due to a HOMO–LUMO transition, where the HOMO is formed by a mixture of metal and dithiolate orbitals while the diimine orbitals give a predominant contribution to the LUMO. This transition is thus termed MMLL′CT (mixed metal-ligand-to-ligand charge-transfer). The negative solvatochromism of this peak and value of $\beta$ is determined by the fact that the charge-transfer axis is collinear but antiparallel to the ground state dipole of the molecule (see Scheme 3, where **A** and **B** reflect the ground and excited CT state, respectively), and thus the excited state is less polar than the ground state. The magnitude of the molecular first hyperpolarizability of several complexes, determined from electric-field-induced second harmonic generation experiments (EFISH) at 1.9 μm, ranges from 0 to $-39 \times 10^{-30}$ esu [28]. Following the simplification the two-state model which takes into account a single excited state, [29] the relationship shown in Eq. (2) can be used to relate the molecular hyperpolarizability ($\beta$) with the transition dipole moment between the first excited and the ground states ($\mu_{ge}$), the difference between the dipole moment of the ground and excited states ($\Delta\mu$) and the energy of the CT absorption band ($E_{ge}$):

$$\beta \propto \frac{\mu_{ge^2}\,\Delta\mu}{(\Delta E_{ge})^2} \qquad (2)$$

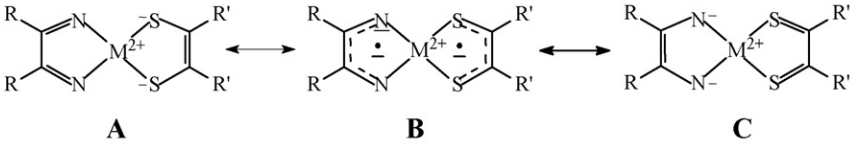
The influence of the variation of the metal, the diimine and the dithiolate on the electronic properties of these complexes have been investigated. The obtained results are satisfactory interpreted by taking into account that substituents on the diimine affect mainly the LUMO, and substituents on the dithiolato affect the HOMO, while the contribution of the metal to the HOMO depends on the metal-dithiolato orbital overlap, and thus on the nature of both of them. Most often the Ni > Pt > Pd $\lambda_{max}$ sequence of the long wavelength has been found. In the series [M(bpy)(bdt)] (bpy = 2,2′-bipyridine, bdt = see Chart 1) the observed Pt > Ni > Pd $\lambda_{max}$ sequence has been explained by taking into account a better metal–ligand overlap of Pt and bdt orbitals [24b].

Moreover it has been shown that Pt-complexes have the highest value of the oscillator strengths suggesting that they are optimal candidates for NLO-applications.

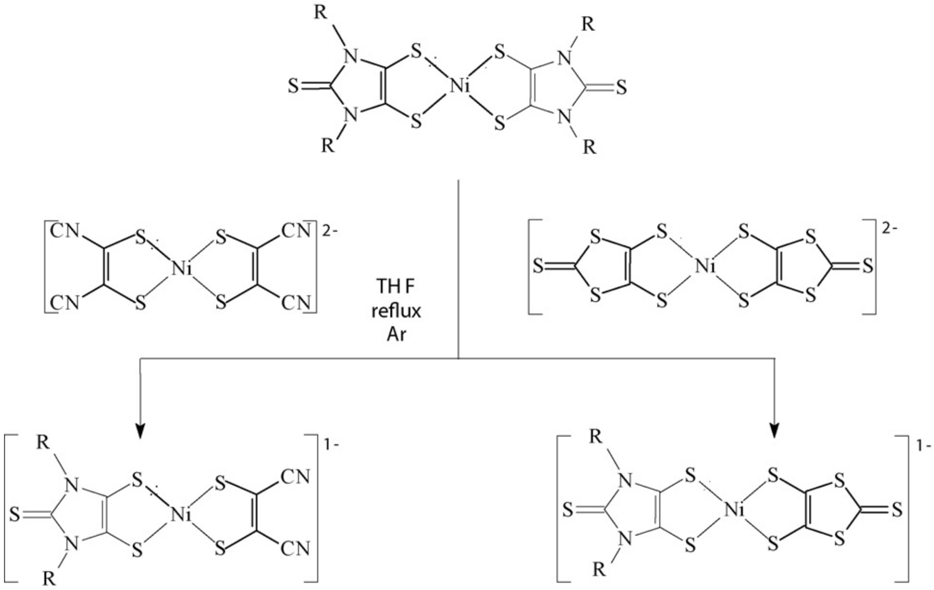
Redox behaviour of the complexes is in general agreement with expectations. In general cyclic voltammograms of these complexes show two reversible reduction waves which are affected by the diimine ligand and one irreversible oxidation wave dependent on the nature of the dithiolate ligand, in agreement with the prevalent contribution of these ligands to the LUMO and HOMO, respectively.

Noteworthy some nickel diimine dithiolate complexes where diimine is diiminosuccinonitrile or 4-benzoyl-o-benzoquinonediimine and dithiolato is tfd show features different to those above described [27]. They exhibit the low energy absorption at longer wavelengths, with relatively large molar absorption coefficients (in the 12,000–19,000 $M^{-1}\,cm^{-1}$ range), small and opposite dipole moment change and unusually small solvatochromic shifts. This behaviour has been explained by taking into account a higher degree of π-delocalization inside the (N=C–C=N)Ni(S–C=C–S) core, influenced by the substituents and reflected by shorter $NiN_2$ and $NiS_2$ distances as compared to similar complexes exhibiting large solvatochromic shifts. This implies that the resonance form **B** of Scheme 3 describes the ground state structure (π-delocalized system). Both the ligands give a significant contribution to the HOMO and the LUMO, and the CT character of the related transition is lost with its potential to provide second order NLO activity to these chromophores.

The influence of the extent of the charge-separated ground state structure on the second order polarizability has been also



**Scheme 3.**



**Scheme 4.**

confirmed in platinum phenanthroline–dithiolate complexes containing sterically demanding groups [30].

In conclusion it has been shown that the properties of $d^8$ metal diimine–dithiolato complexes strongly depend on the degree of π-delocalization inside the (N═C–C═N)Ni(S–C═C–S) core.

## 2. $d^8$ metal mixed-ligand dithiolene complexes

### 2.1. Design and synthesis

Several well documented mixed-ligand dithiolenes of Ni(II) are now available [14,15,19–21,31–38], but they are still much less common compared to the symmetrical counterparts. This is in part relatable to the difficulties encountered in the purification of the products, often contaminated by the symmetrical precursors. Preparative methods are summarized in reactions (6) with yields reported in round parenthesis, and L and L′ indicate ligands with different substituents at the $C_2S_2$ moiety. The reactions involve mainly the nickel ion, but often they are reported to work similarly for the other M = $d^8$ metals(II) despite the fact that Pd and Pt mixed-ligand complexes based on two different dithiolene ligand are still rare [33c,33e,39,40].

$$[\mathrm{Ni(L)_2}] + [\mathrm{Ni(L')_2}]^{2-} \rightarrow 2[\mathrm{Ni(L)(L')}]^{1-} \quad (20\text{–}90\%) \tag{3}$$

$$[\mathrm{M(L)_2}]^{1-} + [\mathrm{M(L')_2}]^{1-} \rightarrow 2[\mathrm{M(L)(L')}]^{1-} \quad (50\text{–}80\%) \tag{4a}$$

$$[\mathrm{Ni(L)_2}] + [\mathrm{Ni(L')_2}] \rightarrow 2[\mathrm{Ni(L)(L')}] \quad (7\text{–}50\%) \tag{4b}$$

$$\mathrm{L}^{2-} + \mathrm{L'}^{2-} + \mathrm{NiCl_2} \rightarrow [\mathrm{Ni(L)(L')}] + [\mathrm{NiL_2}] + [\mathrm{NiL'_2}] \quad (0.8\text{–}21\%) \tag{4c}$$

$$[\mathrm{M(L')(NH_3)_2}] + \mathrm{L} \rightarrow [\mathrm{M(L)(L')}] \quad (60\%) \tag{5a}$$

$$[\mathrm{M(L)(X)_2}] + (\mathrm{L'})^{2-} \rightarrow [\mathrm{M(L)(L')}] \quad (40\%) \tag{5b}$$

$$[\mathrm{Ni(L)_2}]^{2+} + [\mathrm{Ni(L')_2}]^{2-} \rightarrow 2[\mathrm{Ni(L)(L')}] \quad (> 90\%) \tag{6a}$$

$$[\mathrm{Ni(L)_2}]^{2+} + [\mathrm{Ni(L')_2}]^{1-} \rightarrow [\mathrm{Ni(L)(L')}] + [\mathrm{Ni(L')_2}] \quad (> 90\%) \tag{6b}$$

In reaction (3) and Scheme 4, $[\mathrm{NiL'_2}]^{2-}$ can work as reducing agent towards $[\mathrm{NiL_2}]$ with formation of symmetrical monoanionic intermediates which react to produce the mixed-ligand compound through a scrambling reaction, as shown in reaction (4a) [19]. Methods (4a)–(4c) are based on scrambling reactions, and separation procedures are required to isolate the mixed-ligand complex when equilibrium mixtures of asymmetrical and symmetrical precursors are formed [31–33]. Moreover scrambling reactions can also been complicated by competing redox reactions of the symmetrical precursors and/or ligand substitutions reactions. These complications were recognized since the early studies by McCleverty and co-workers, which were able to isolate mixed-ligand complexes by mixing the symmetrical complexes based on the ligands L = dpedt, L′ = tdf and mnt (see Chart 1) through reaction (4a) obtaining satisfactorily pure salts of the $[\mathrm{Ni(dpedt)(tfd)}]^{1-}$ and $[\mathrm{Ni(dpedt)(mnt)}]^{1-}$ anionic complexes [31a]. Rapidity in the isolation and purification of the mixed-ligand complexes was recommended to avoid the formation of an equilibrium mixture between asymmetrical and symmetrical complexes. Also, the role of the solvent in determining the reaction yields was discussed.

Salts of the following anionic mixed-ligand dithiolenes: $[\mathrm{M(dmit)(mnt)}]^{1-}$ (M = Ni, Pd and Pt); $[\mathrm{Ni(dddt)(mnt)}]^{1-}$; $[\mathrm{Ni(ddds)(mnt)}]^{1-}$; $[\mathrm{Ni(dsit)(mnt)}]^{1-}$; $[\mathrm{Ni(dmse)(mnt)}]^{1-}$; $[\mathrm{Ni(dddt)(dmit)}]^{1-}$; $[\mathrm{Ni(ddds)(dmit)}]^{1-}$; $[\mathrm{Ni(dmio)(dmit)}]^{1-}$$[\mathrm{Ni(tdas)(dmit)}]^{1-}$; $[\mathrm{Ni(tdas)(ddds)}]^{1-}$ (see Chart 1), have been obtained in yields varying in the 50–80% range by purifying the products of the scrambling reaction (4a) with a reversed phase column chromatography, using acetonitrile/water as eluent. No back reaction into the symmetrical complexes has been observed. This method is reported to work well for the M(II) = Ni, Pd, Pt triad [32a]. Electrochemical data of five examples of these mixed-ligand complexes have shown these data are intermediate between those of symmetrical precursors. Thanks to the tuning of their electrochemical properties, these mixed-ligand complexes provide suitable candidates to be used as counterions to prepare CT salts based on tetrathiafulvalene-cations derivatives. Among these salts those having $[\mathrm{Ni(dmit)(mnt)}]^{1-}$ and $[\mathrm{Ni(tdas)(dmit)}]^{1-}$ as counterions show metallic behaviour down to 20–30 K [32b]. Neutral mixed-ligand complexes [Ni(edo)L′] (L′ = dddt, ddds, ddt, pdt, dmtdt; see Chart 1) have been prepared in refluxing DCE through the scrambling reaction (4b) in low to moderate yield, with the view to tailoring electrochemical properties and solubili-

**Table 1**
Selected bond distances (Å) and angles (°) for [MLL′] mixed-ligand complexes.

| [MLL′] | M–S(L)[a] | C–S(L′)[a] | C–C(L) | M–S(L′)[a] | C–S(L′)[a] | C–C(L′) | Ref |
|---|---|---|---|---|---|---|---|
| M = Ni, L = $Me_2$pipdt; L′ = mnt | 2.162(2) | 1.700(6) | 1.433(3) | 2.146(2) | 1.735(6) | 1.32(1) | [20] |
| M = Ni, L = $Et_2$pipdt; L′ = mnt | 2.170(2) | 1.700(6) | 1.436(11) | 2.152(2) | 1.731(8) | 1.338(10) | [34] |
| M = Pd, L = $Et_2$timdt; L′ = mnt | 2.2580(8) | 1.658(3) | 1.453(4) | 2.3297(8) | 1.732(3) | 1.354(4) | [39] |
| M = Ni, L = *c*$Dod_2$pipdt; L′ = mnt | 2.165(3) | 1.675(11) | 1.50(2) | 2.145(3) | 1.732(12) | 1.34(2) | [21] |
| M = Ni, L = $Me_2$dazdt; L′ = mnt | 2.189(2) | 1.693(7) | 1.471(8) | 2.146(2) | 1.734(8) | 1.345(10) | [37] |
| M = Ni, L = $Et_2$dazdt; L′ = mnt | 2.196(1) | 1.699(3) | 1.444(4) | 2.151(1) | 1.735(3) | 1.351(4) | [34] |
| M = Ni, L = $Pr^i_2$pipdt; L′ = dmit | 2.163(1) | 1.691(2) | 1.480(3) | 2.159(1) | 1.733(2) | 1.344(3) | [15] |
| M = Ni, L = $Bz_2$pipdt; L′ = dmit | 2.148(1) | 1.691(2) | 1.477(3) | 2.163(1) | 1.731(2) | 1.349(3) | [25] |
| M = Pd, L = $Me_2$pipdt; L′ = dmit | 2.252(1) | 1.676(7) | 1.516(12) | 2.242(1) | 1.722(7) | 1.388(12) | [40] |
| M = Ni, L = $Me_2$pipdt; L′ = dddt | 2.160(2) | 1.687(7) | 1.470(8) | 2.149(2) | 1.744(6) | 1.335(8) | [35] |
| M = Ni, L = $Pr^i_2$timdt; L′ = dmit | 2.173(2) | 1.694(6) | 1.387(1) | 2.147(2) | 1.744(6) | 1.29(1) | [19] |
| M = Ni, L = pddt; L′ = dmio | 2.125(2) | 1.709(4) | 1.388(5) | 2.148(2) | 1.698(4) | 1.372(6) | 33f |
| M = Ni, L = dpedt; L′ = dmio | 2.119(1) | 1.704(4) | 1.404(5) | 2.144(1) | 1.696(4) | 1.380(5) | 33g |
| M = Ni, L = edo; L′ = dmit | 2.14(5) | 1.68(4) | 1.40(7) | 2.14(5) | 1.70(4) | 1.39(7) | 32c |
| M = Ni, L = tmedt; L′ = dmit | 2.151(2) | 1.685(5) | 1.379(8) | 2.149(2) | 1.694(4) | 1.387(7) | 33g |
| M = Ni, L = dmeds; L′ = dmit | 2.298(2) | 1.859(6) | 1.356(8) | 2.194(2) | 1.704(6) | 1.371(8) | 33a |
| M = Ni, L = tmedt; L′ = dddt | 2.150(1) | 1.687(4) | 1.375(6) | 2.127(1) | 1.710(4) | 1.386(5) | 33g |
| M = Ni, L = dpedt; L′ = dddt | 2.117(1) | 1.705(3) | 1.391(4) | 2.129(1) | 1.708(1) | 1.380(4) | 33g |
| M = Ni, L = dtmopedt; L′ = tdf | | 1.710(4) | 1.410(5) | | 1.712(4) | 1.366(6) | [21] |

[a] Average value.

ties to prepare radical-cation salts, which are interesting for their electroconducting properties. An equilibrium mixture between reagents and product is formed, and, as cited above, this leads complications in the isolation of pure mixed-ligand complexes. Two other mixed-ligand complexes [Ni(edo)L′] (L′ = dmit and mnt) have been obtained serendipity in the electrolysis of solutions containing $[Ni(edo)_2]$ and $Bu^n{}_4N[NiL'_2]$ [32c].

Reaction (4c) is based on the cross-coupling method proposed by Papavassiliou's group [33] with the view to obtain single-components semiconductors or NLO chromophores. Again, the formation of an equilibrium mixture between reagents and product requires purifying procedures based on column chromatography, giving yields from very low to moderate values. Several mixed-ligand complexes: [Ni(dmeds)(dmit)], [Ni(dmedt)(dmit)], [Ni(dpedt)(dsit)], [Ni(dpedt)(dmit)], [Ni(dctdt)(dmit)] [33a]; [Ni(dmedt)(dmio)] [Ni(dmstfdt)(dmio)] [33b]; [M(dpedt)(dddt)] (M = Pd, Pt, Au); [Pd(dpedt)(dmit)] [33c]; [Ni(edt)(dmio)], [Ni(edt)(dmit)], [Ni(dctdt)(dmit)] [33d], [M(edt)(dddt)] (M = Ni, Pd) [33e] have been isolated and in some instances structurally characterized (see Table 1).

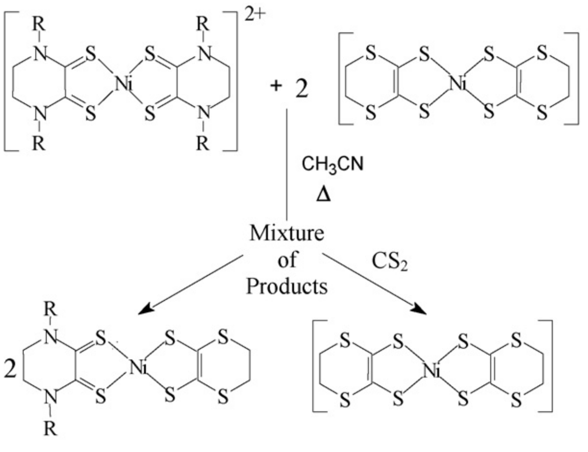
Method (5a) is based on the substitution reaction of two $NH_3$ groups with a dithione chelating ligand and requires the availability of the precursor $[M(L')(NH_3)_2]$ and of a stable dithione ligand [21,34]. Method (5b) is based as well on a substitution reaction, which can be taken as the counterpart of (5a), where the starting complex is coordinated to a formal dithione: $[Pd(Et_2timdt)(Br)_2]$ while one dithiolato chelating ligand substitutes the two bromides [39].

Methods (6a) and (6b) are very effective, giving almost quantitative yields of the mixed-ligand complexes, and can be employed where cationic and anionic complexes are available. While several stable anionic complexes are known, the cationic dithiolenes are uncommon. Among these the class of $[M(L)_n]^{2+}$ ($n = 2$, M = Ni, Pd, Pt, L = $R_2$pipdt; $n = 3$, M = Ni, L = $R_2$dazdt) have proved to be suitable precursors to prepare in almost quantitative yields mixed-ligand derivatives (L = $R_2$pipdt) [15,20,36,40] (L = $R_2$dazdt) [37] by reacting with Ni-dianionic dithiolenes.

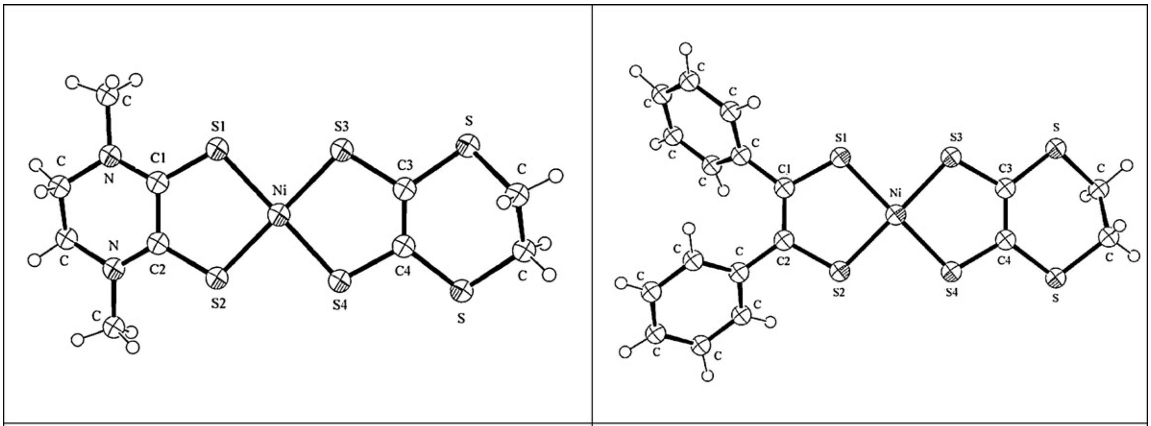
This reaction can work also by using monoanionic complexes, when the complexes are more easily available in this state. As shown in Scheme 5, the monoanion undergoes dismutation producing the neutral species and the dianionic one which is consumed to produce the mixed-ligand complex [35]. Separation procedures are required to isolate the mixed-ligand complex in pure form from the symmetrical neutral species.

No one of the listed methods is suitable for a general application. In fact since the high or low difference in the *push*/*pull* character of the two ligands in mixed-ligand complexes will give rise to a predominant asymmetric or symmetric distribution of the charge at the $[(C_2S_2)M(C_2S_2)]$ core [9], the most suitable preparation method will depend on the desired nature of the mixed-ligand products and related properties. In order to evaluate the *push*/*pull* character of the ligands, the negative or positive value of $E_{1/2}{}^0$ for the reduction 0/1− process may be used, being this value relatable to the stability of the oxidized or reduced species. Thus complexes with increasing strong *push* ligands exhibit increasing negative $E_{1/2}{}^0$ for the reduction steps starting from 2+/1+, and derivatives with highly *pull* substituents increasing positive $E_{1/2}{}^0$ for the 1−/2− process. By taking into accounts the literature available data the following sequences of increasing *push*: $R_2$timdt < dmedt < $R_2$pipdt; and *pull*: dpedt < dddt < edt < 3,5-*t*-$Bu_2$bdt < dmit < tfpedt < tdas < tfd < mnt <dtcr character can be proposed [9].

Methods (4a)–(4c) which use symmetrical complexes accessible in the same status, having similar *push*/*pull* character of the ligands, are appropriate to prepare mixed-ligand complexes with extensive π-delocalization and properties intermediate between those of symmetrical precursors. The formation of the product is mostly relatable to the random reorganization process and separation procedures are required to isolate the mixed-ligand complex from the



**Scheme 5.**



| **[Ni(Me$_2$pipdt)(dddt)]** | [Ni(dpedt)(dddt)] |
|---|---|
| Me$_2$pipdt: d(CS) 1.687(7) Å; d(C1C2) 1.470(8) Å | dpedt: d(CS) 1.705(3) Å; d(C1C2) 1.391(4) Å |
| dddt: d(CS) 1.744(6) Å; d(C3C4) 1.335(8) Å | dddt: d(CS) 1.708(1) Å; d(C3C4) 1.380(4) Å |

**Fig. 2.** Molecular structures and most significant bond distances of [Ni(Me$_2$pipdt)(dddt)] and [Ni(dpedt)(dddt)] as examples of a predictable π-localized and π-delocalized system respectively.

symmetrical precursors. Low to intermediate reaction yields are predictable. These complexes can be of interest for tuning solubility and/or electronic properties of symmetrical precursors to optimize that for applications such as NIR dyes or precursors of electroconducting CT salts.

When π-localized mixed-ligand complexes, suitable as second order NLO chromophores, are desirable methods (5) and (6) can be employed. In these cases the *push*/*pull* character of the ligands of the symmetrical precursors is significantly different so that they can be describable as dithione and dithiolato. The formation reaction is very effective.

On variation of *push*/*pull* character of the ligands between these two limiting cases, a gradual variation of the π-electron distribution from the fully delocalized to localized case and related properties is predictable.

In conclusions the knowledge of the factors which govern the π-electron distribution in $d^8$ mixed-ligand dithiolene complexes will allow chemists to tailor species to show greater or lower second order nonlinear activity. The potential as second order NLO chromophores of this class of complexes, where one ligand is reducing and the other is oxidizing, similarly to what happens in the diimine–dithiolato case, was recognized by Vogler and Kunkely since early 1980s [38]. However, preliminary measurements on $[\mathrm{Ni(mnt)(dpedt)}]^{1-}$ seemed not much promising being the solvent dependence of the low energy absorption much smaller than what generally observed in the diimine–dithiolato cases. However, it must be considered that very low charge separation occurs in the complex in its stable monoanionic form. By using nickel complexes stable in neutral form and using ligands with significantly different *push*/*pull* character [14,15,21,35,40] large negative solvatochromism and molecular first hyperpolarizability ($\beta$) comparable or higher than in the diimine–dithiolato cases have been found [26–28].

### 2.2. Structural features

Selected structural data on mixed-ligand complexes are reported in Table 1. The metal is coordinated by the four S-atoms in a square-planar environment, and four similar M–S distances are generally found. In the Ni(II) case, the four Ni–S coordination bonds fall in the 2.148–2.173 Å range irrespective of the *push*/*pull* character of the ligands. This suggests that the Ni–S σ bonds are more or less equivalent and that Ni–S π-interactions are of minor importance. Interestingly in [Pd(Et$_2$timdt)(mnt)], significantly shorter and longer Pd–S bond distances are instead found. The comparison of the C–C and C–S bond distances in the C$_2$S$_2$ units seem more useful to highlight a different electronic distribution at the ligands. In some cases the C–S and C–C distances are significantly longer and shorter respectively in the two ligands (for example [Ni(Me$_2$pipdt)(dddt)]; [Ni(Pr$^i{}_2$pipdt)(dmit)]; [Ni(Me$_2$dazdt)(mnt)]; ...). Accordingly, structural data reflect a localized π electron distribution for these complexes (limiting structures **A** or **C** in Scheme 2) in agreement with the *pull* character (dithiolate) for mnt, dmit and dddt ligands and the *push* character (dithione) for R$_2$pipdt and Me$_2$dazdt ones. In other cases the C–S and C–C distances are similar in the two ligands (for example [Ni(dpedt)(dddt)]; [Ni(tmedt)(dmit)]; [Ni(dpedt)(dmio)]; ...).

Accordingly, structural data reflect a delocalized π-electron distribution for these complexes (**B**, equivalent contribution of limiting structures **A** and **C** in Scheme 2) in agreement with the similar *push*/*pull* character of the ligands. In Fig. 2 the molecular structures of [Ni(Me$_2$pipdt)(dddt)] and [Ni(dpedt)(dddt)] are shown as examples of a predictable π-localized and π-delocalized system respectively.

The stacking of molecules in the solid state strongly depends on the nature of the ligands and their capability to interact through π–π and/or van der Waals interactions, as well as donor–acceptor and H-bonding. Most of the mixed-ligand complexes which have been structurally solved, crystallize in a centrosymmetric space group. This is detrimental for the possible use of these solids as second order NLO materials. Actually, in addition to the requirements to be a polarizable material with asymmetric charge distribution accompanied by a π-conjugated electron pathway, an acentric crystal packing is required in order that the crystals have SHG activity. Recently some examples of mixed-ligand complexes [M(dpedt)(dddt)] (M = Ni, Pd, Pt, Au) [33c,33g]; and [Ni(dpedt)(pddt)] [41] have been reported to crystallize with the non-centrosymmetric space group *Pbc2$_1$*. However no molecular second order NLO activity has been determined for these compounds and structural data seem to suggest a symmetric charge distribution. Thus at the moment, unfortunately, the most suitable mixed-ligand complexes at molecular level give centrosymmetric crystals, while the less suitable at molecular level give non-centrosymmetric crystals!

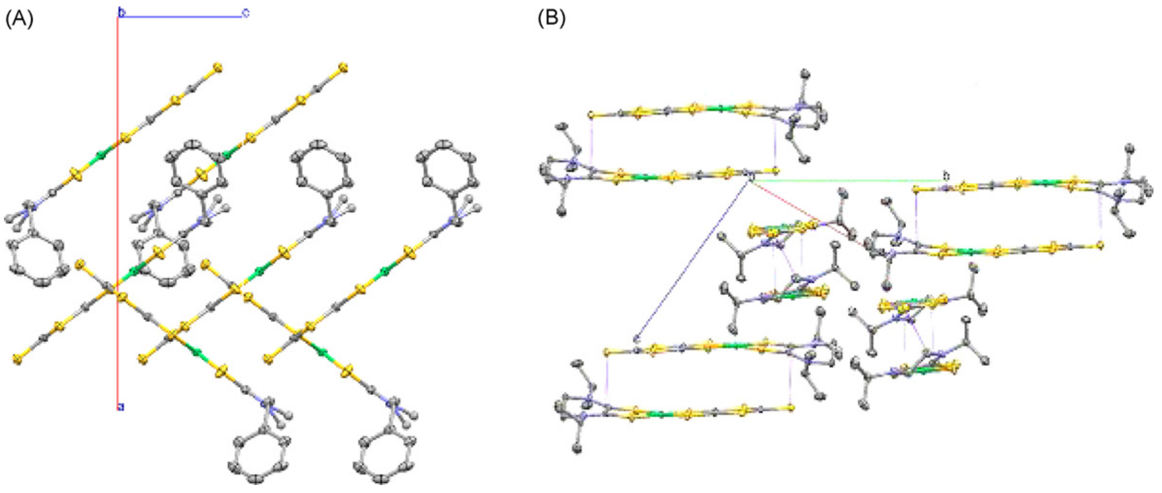


**Fig. 3.** Comparison of packing motifs in [Ni(Bz$_2$pipdt)(dmit)] (**A**) where the molecules form a one-dimensional structure and [Ni(Pr$^i{}_2$pipdt)(dmit)] (**B**) where the molecules are head-to-tail with each other forming dimers.

The introduction of chiral substituents in the more promising molecular second order NLO chromophores should promote the formation of desired non-centrosymmetric crystals.

The stacking of molecules in the solid state is also of crucial importance in determining the bulk material electroconducting properties, which are object of another review article of this special issue by N. Robertson. In Fig. 3 the stacking motifs of [Ni(R$_2$pipdt)(dmit)] on variation of the R group from Pr$^i$ to benzyl are shown [25]. The latter shows a uniform one-dimensional stack with an interplanar distance of 3.65(1) Å, which is typical of π-stacked metal-dithiolene complexes, rather than the strongly dimerized motifs of the former. This is reflected in the diffuse reflectance spectra of the complexes as well as for band dispersion similar to that observed for example in [Ni(dmit)$_2$]. This suggests potential for these complexes as conducting materials when suitably doped, and also a further possibility to tune the solid-state properties by variation of the R group through one ligand, whilst maintaining the functionality of the molecule.

### 2.3. *ν(C=C) as vibrational marker for ligand's redox state*

IR and Raman data well complement structural findings and, in the absence of detailed vibrational studies, the C=C stretching frequency provides the most useful vibrational marker of the redox state of the ligands since it is generally easy to be detected in both IR and Raman spectra. In symmetrical $d^8$-M(II) dianions, the C=C bond region of the ligand is bonding in the HOMO (π orbital), while this orbital is not populated in the neutral M(II) complexes. This is reflected by increasing C=C bond lengths and decreasing C=C stretching frequencies with decreasing number of electrons, in agreement with the redox-active frontier orbitals whose composition is predominantly ligand based. This allows to relate the frequency of C=C stretchings with the charge of $d^8$ metal-dithiolenes. For dmit and dddt symmetrical complexes, where several examples of complexes with different charge are available, a linear dependence of the totally symmetric stretching vibration frequency with the charge has been found [42,43].

For the more limited cases of mnt redox derivatives, the C=C vibration assigned to the monoanion and dianion is generally found at approximately 1440 and 1490 cm$^{-1}$, respectively [44]. In Table 2 a list of the available IR and Raman peaks of mixed-ligand complexes relatable to the C=C stretching vibrations are reported.

In Fig. 4 the linear correlation between the frequency of C=C stretchings with the charge for dmit and dddt based complexes is shown. Through this correlation the redox state of the ligand can be evaluated and, in agreement with structural data, it helps to predict whether the complexes are better describable as either

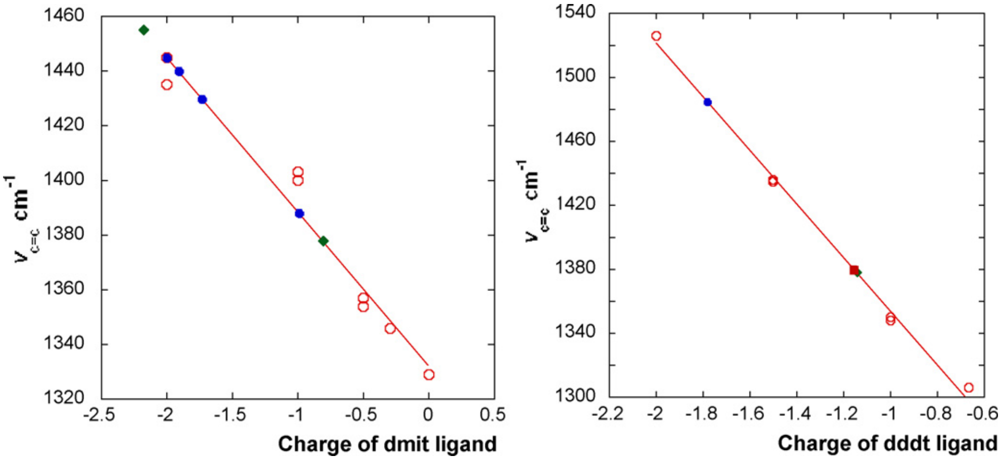


**Fig. 4.** ν(C=C) stretching vibrations vs charge of dmit and dddt complexes (correlation coefficient > 0.998). Points (○) refer to data for symmetrical complexes taken from references [42,43] respectively. Points (●), (◆) and (■) refer respectively to the Raman or IR peaks of the nickel, palladium and platinum mixed-ligand complexes listed in Table 2.

**Table 2**
Raman (R) or infrared peaks (IR) relatable to C=C stretching vibrations in $d^8$ mixed-ligand dithiolene complexes based on mnt, dmit, dddt ligands.

| Complexes | $\nu$(C=C) cm$^{-1}$ | Charge of ligand[a] | Ref. |
|---|---|---|---|
| [Ni(Me$_2$pipdt)(mnt)] | 1492 (R) | ≈−2 mnt | [20] |
| [Ni(Pr$^i{}_2$timdt)(mnt)] | 1425 (R) | ≈−1 | [19] |
| [Pd(Et$_2$timdt)(mnt)] | 1485 (R) | ≈−2 | [39] |
| [Pd(Me$_2$pipdt)(dmit)] | 1455 (R) | −2.2 dmit | [40] |
| [Ni(M$_2$pipdt)(dmit)] | 1430 (R) | −1.7 | [20] |
| [Ni(Pr$^i{}_2$pipdt)(dmit)] | 1440 (R) | −1.9 | [15] |
| [Ni(Ph$_2$pipdt)(dmit)] | 1445 (R) | −2.0 | [45] |
| [Ni(Pr$^i{}_2$timdt)(dmit)] | 1388 (R) | −1.0 | [19] |
| [Pd(dpedt)(dmit)] | 1378 (IR) | −0.8 | 33c |
| [Ni(Me$_2$pipdt)(dddt)] | 1485 (R) | −1.8 dddt | [35] |
| [M(dpedt)(dddt)] (M = Pd, Pt) | 1380 (IR) | −1.1 | 33c |

[a] This is the formal charge evaluated through the linear correlations shown in Fig. 4 for dmit and dddt ligands, and for mnt by comparison with the corresponding peaks of the di- and monoanions.

π-delocalized (dithiolenes) or π-localized (dithione–dithiolato) systems.

## 2.4. Electronic spectroscopy

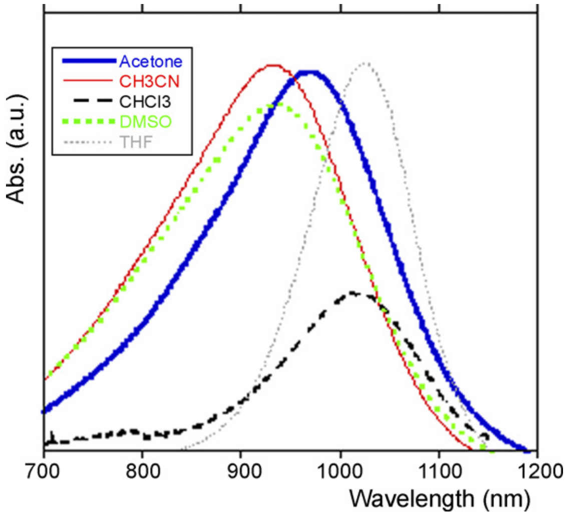


**Fig. 5.** NIR spectra of [Ni(Me$_2$pipdt)(dddt)] in different solvents.

The mixed-ligand complexes based on R$_2$pipdt and R$_2$dazdt *push* ligands are characterized in the visible region by one or two moderately strong long wavelength absorptions ($\varepsilon$ in the 2300–11,800 mol$^{-1}$ dm$^3$ cm$^{-1}$ range) which show strong solvatochromic shift negative in sign, as shown in Fig. 5 for the [Ni(Me$_2$pipdt)(dddt)] case as an example [35]. Where although asymmetric, the complexes have comparable electron-withdrawing capability of the two different ligands, the mixed-ligand complexes the vis–NIR peaks shift to higher wavelengths, have high molecular absorptivities ($\varepsilon$ in the 22,000–45,000 M$^{-1}$ cm$^{-1}$ range), and show moderate solvatochromic shift, in some instances positive in sign. Where the spectra of symmetrical neutral precursors are available this peak falls at intermediate values (Table 3).

As described in Section 1.2 a π → π* HOMO–LUMO transition is responsible for the vis–NIR absorption. Where the electrowithdrawing capability of the two ligands is different, the HOMO has prevailing contribution from the dithiolato (*pull*) ligand, and the LUMO prevailing dithione (*push*) contribution. The mixing of metal orbitals with the frontier orbitals may give mixed metal–ligand to metal–ligand character to the HOMO–LUMO CT transition. This is

**Table 3**
Electronic spectra of the complexes [NiLL′].

| | $\lambda_{max}$(nm) | $\varepsilon \times 10^{-3}$ (M$^{-1}$cm$^{-1}$) | $\lambda_{max}$(nm) | $\varepsilon \times 10^{-3}$ (M$^{-1}$ cm$^{-1}$) | Ref. |
|---|---|---|---|---|---|
| [Ni(Pr$^i{}_2$pipdt)(dmit)][a] | | | 965 | 11.0 | [20] |
| [Ni(Me$_2$pipdt)(mnt)][a] | | | 733 | 4.0 | [15] |
| [Ni(Me$_2$pipdt)(tdas)][b] | 621 | sh | 729 | 4.2 | [45] |
| [Ni(Me$_2$pipdt)(qxd)][b] | 591 | sh | 722 | 5.0 | [45] |
| [Ni(Me$_2$pipdt)(dtcr)][b] | 615 | 2.5 | 710 | 2.6 | [45] |
| [Ni(Ph$_2$pipdt)(dtcrCN)][b] | 653 | 4.0 | 784 | 6.8 | [45] |
| [Ni(Me$_2$pipdt)(dmit)][c] | 744 | sh | 820 | 6.9 | [45] |
| [Ni(Me$_2$pipdt)(dsit)][c] | 716 | sh | 810 | 7.5 | [45] |
| [Ni(Pr$^i{}_2$pipdt)(dmit)][c] | 742 | sh | 833 | 6.0 | [45] |
| [Ni(Ph$_2$pipdt)(dmit)][c] | | | 912 | 11.3 | [45] |
| [Ni(Me$_2$pipdt)(dddt)][b] | | | 930 | 11.7 | [35] |
| [Ni(Me$_2$dazdt)(mnt)] | 598 | 3.1 | 800 | 2.1 | [45] |
| [Ni(Me$_2$dazdt)(dtcr)] | 576 | 6.8 | 745 | 2.3 | [45] |
| [Ni(Pr$^i{}_2$timdt)(dmit)][d] | | | 1056 | 39.8 | [19] |
| [Ni(Pr$^i{}_2$timdt)(mnt)][b] | | | 883 | 24.1 | [20] |
| [Pd(Et$_2$timdt)(mnt)][a] | | | 1064 | 13.0 | [39] |
| [Ni(edt)(dddt)][e] | | | 864 | n.a. | 33e |
| [[Ni(edt)$_2$][e] | | | 719 | n.a. | 33e |
| [Ni(dddt)$_2$][e] | | | 1015 | n.a. | 33e |
| [Pd(dpedt)(dddt)][d] | | | 980 | 40.7 | 33c |
| [Pt(dpedt)(dddt)][d] | | | 906 | 44.7 | 33c |
| [Ni(edt)(dmio)][d] | | | 830 | 17.7 | 33d |
| [Ni(dmdt)(dmio)][d] | | | 977 | 38.0 | 33b |
| [Ni(dmstfdt)(dmio)][d] | | | 988 | 36.3 | 33b |
| [Ni(edt)(dmit)][d] | | | 906 | 21.7 | 33d |
| [Ni(dmedt)(dmit)][d] | | | 933 | 29.1 | 33d |
| [Ni(dpedt)(dmit)][d] | | | 974 | 44.6 | 33d |
| [Pd(dpedt)(dmit)][d] | | | 1000 | 39.8 | 33c |
| [Ni(dcdt)(dmit)][d] | | | 1040 | 34.7 | 33d |

[a] In CHCl$_3$.
[b] In CH$_3$CN.
[c] In DMF.
[d] In CS$_2$.
[e] In MeOH.

in agreement with the observed trend of $\lambda_{max}$ on varying the *pull* ligand at parity of the *push* ligand. It is found that the wavelength decreases with the electrowithdrawing capability of the *pull* ligand: $[Ni(R_2pipdt)(L')]$ ($\lambda_{max}$ in nm) L′ = mnt (733, $CH_3CN$); tdas (729, $CH_3CN$); dtcr (710 in $CH_3CN$); dsit (810 in DMF); dmit (820 in DMF); dddt (930 in $CH_3CN$). A significant number of examples on variation of the *push* ligand and of the metal are required to evaluate their influence on the electronic properties of the mixed-ligand complexes. Results on the limited cases so far investigated by our group suggest that $\lambda_{max}$ follows the order Ni > Pt > Pd. The observed features are similar to those exhibited by $d^8$ metal diimino–dithiolato complexes (see Section 1.3) [23,24,27,28,30,46].

In complexes where the ligands have comparable electron-withdrawing capability, the HOMO–LUMO transition will not have CT character, no second order NLO activity is predictable and observed where these measurements are available. These complexes behave as NIR dyes whose properties are intermediate to those of the symmetrical counterparts.

### 2.5. Cyclic voltammetry

Cyclic voltammetric data for some asymmetrical nickel complexes and for some symmetrical precursors are presented in Table 4. Complexes based on $R_2$pipdt and $R_2$timdt as *push* ligands and dmit, tdas and mnt as *pull* ligands show two reversible reduction waves at progressively negative potentials and one irreversible oxidation wave.

The one-electron oxidation potentials ($E_a$) are relatable to the energy of the HOMO, in addition to the spin pairing energy of the electrons in this level. The sequence of oxidation potentials suggests that the removal of one electron is a more easy process for the dmit- and a more difficult one for mnt-based complex in the investigated range. This is consistent with spectroscopic findings and the expected composition of the frontier orbitals where the ligand acting as dithione gives a higher contribution to the LUMO and the ligand acting as dithiolato to the HOMO (see also Section 2.6; Fig. 6).

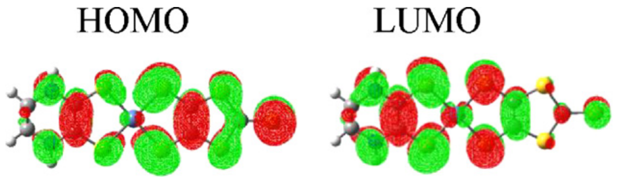


**Fig. 6.** Frontier orbitals calculated for the model $[Ni(H_2pipdt)(dmit)]$ compound showing the unbalanced atomic contributions of the two ligands, and the scarce contribution of the terminal $CS_3$ moiety of dmit to the LUMO.

Again, where although asymmetric, the ligands have comparable electron-withdrawing capability the redox properties of the mixed-valence complexes are intermediate between those of symmetrical precursors. Similarly optical and electrochemical properties intermediate between those of symmetrical precursors have been observed in metal-dithiolenes where the same ligand bears two different substituents such as 2-(trifluoromethyl)acrylonitrile-1,2-dithiolate or 2-cyano-1,2-ethane dithiolate [47] or cis-1-(2′-thienyl)-2-phenyl-1,2-ethenedithiolate [48] or also where the ligand is asymmetric, such as in the case of N-methyl-1,3-thiazoline-2-thione-5,5-dithiolate and diselenolate [49].

### 2.6. Second order NLO properties and dipole analysis

A summary of second order NLO data and of dipole analysis on some examples so far available in literature for nickel mixed-ligand dithiolenes are reported in Table 5.

The complex $[Ni(R_2pipdt)(mnt)]$, with R = 2-ethylhexyl associates a large ground state dipole moment ($\mu_g = 16$ D) to negative solvatochromism ($\beta_0 = -37 \times 10^{-30}$ esu, is the zero-frequency value of the molecular hyperpolarizability) [53].

The complex $[Ni(Pr^i_2pipdt)(dmit)]$ shows a higher negative $\beta_0$ value ($\beta_0 = -130 \times 10^{-30}$ esu) while the $\mu_g$ value is slightly smaller (13 D). In both cases, it may be assumed that the π-localized dithione–dithiolato structure (type **A**, in Scheme 2) is prevailing in the ground state and that the dipole moment is directed from $Pr^i_2$pipdt toward the *pull* ligand (mnt or dmit). Upon the CT transition (excited state), the separation of charges could be quenched or even inverted. According to Eq. (2) the two-level model (to estimate the first molecular hyperpolarizability from the lowest

**Table 4**
Cyclic voltammetric data[a] of some asymmetrical $[NiLL']^n$ complexes and symmetrical precursors.

| Compound | $E_a$ (V)[b] $ML_2^0 \rightarrow ML_2^{1+} + e^-$ | $E_{1/2}$ (V)[c] $ML_2^0 + e^- \rightleftharpoons ML_2^{1-}$ | $E_{1/2}$ (V)[c] $ML_2^- + e^- \rightleftharpoons ML_2^{2-}$ | Ref. |
|---|---|---|---|---|
| $[Ni(Pr^i_2timdt)_2]$ | +0.78[c] | −0.100[d] | −0.598 | [9] |
| $[Ni(tdas)_2]^{2-}$ | | +0.80[b] | +0.18 | [50] |
| $[Ni(dmit)_2]^{2-}$ | | +0.316[b] | −0.109 | [19] |
| $[Ni(mnt)_2]^{2-}$ | | +1.110[b] | +0.270 | [19] |
| $[Ni(dddt)_2]^{2-}$ | | +0.105 | −0.645 | [51] |
| $[Ni(Pr_2{}^itimdt)(dmit)]^{1-}$ | +1.154 | n.o.[e] | −0.402 | [15] |
| $[Ni(Pr_2{}^itimdt)(mnt)]$ | +1.160 | +0.354 | −0.307 | [15] |
| $[Pd(Et_2timdt)(mnt)]$ | +1.41 | +0.39 | −0.29 | [39] |
| $[Ni(Pr^i_2pipdt)(dmit)]$ | +0.590 | −0.593[d] | −1.165[d] | [15] |
| $[Ni(Me_2pipdt)(mnt)]$ | +0.900 | −0.530 | −0.970 | [20] |
| $[Ni(Me_2pipdt)(tdas)]$ | +0.820 | −0.582 | −1.034 | [20] |
| $[Ni(mnt)(dmit)]^{1-}$ | | +0.73[b] | +0.06 | 32a |
| $[Ni(mnt)(dddt)]^{1-}$ | | +0.51[b] | −0.26 | 32a |
| $[Ni(dddt)(dmit)]^{1-}$ | | +0.23[b] | −0.38 | 32a |
| $[Ni(edt)_2]^{2-}$ | | +0.135 | −0.905 | [52] |
| $[Ni(edt\text{-}CN)_2]^{2-}$ | | +0.695 | −0.265 | 47b |
| $[Ni(tfd)_2]^{2-}$ | | +0.53[f] | −0.51[f] | 47a |
| $[Ni(mnt)_2]^{2-}$ | | +0.63[f] | −0.16[f] | 47a |
| $[Ni(tfadt)_2]^{2-}$ | | +0.51[f] | −0.45[f] | 47a |

[a] The measured values have been reported vs Ag/AgCl sat. as reference electrode.
[b] Irreversible.
[c] Reversible.
[d] Quasi-reversible one-electron reduction.
[e] Not observed.
[f] $E$ vs $Fc/Fc^+$.

**Table 5**
Optical data and dipole analysis of asymmetrical [NiLL′] complexes.

| [NiLL′] | $\lambda_{max}$ (nm) $10^3\varepsilon$ ($M^{-1}$ $cm^{-1}$) | $\mu_{eg}$ (D) | $\mu_g$ (D) | $\mu_e - \mu_g$ (D) | $10^{-30}\beta_0$ (esu) | Ref. |
|---|---|---|---|---|---|---|
| L = $(EH)_2$pipdt L′ = mnt | 829; 9.8 | 3.7 | 16 | −10 | −37 | [21] |
| L = $(EH)_2$pipdt; L′ = tdf | 840; 8.7 | 3.6 | 13 | −8 | −20 | [21] |
| L = dtmopedt; L′ = tfd | 842; 19.0 | 5.9 | 6 | 1 | +5 | [21] |
| L = $Pr^i{}_2$timdt; L′ = mnt | 883; 24.1 | 6.7 | 16 | ∼0 | ∼0 | [19] |
| <H7 > L = $Pr^i{}_2$pipdt; L′ = dmit | 965; 10.9 | 5.9 | 13 | −11 | −130 | [20] |

$\beta_0$ = zero-frequency term of $\beta$, D = Debye.

optically allowed HOMO–LUMO excitation) [14], the negative sign of $\beta$ depends on $\mu_e < \mu_g$, the other parameters (dipole transition moment, $\mu_{ge}$ and energy gap $\Delta E_{ge}$) being both squared.

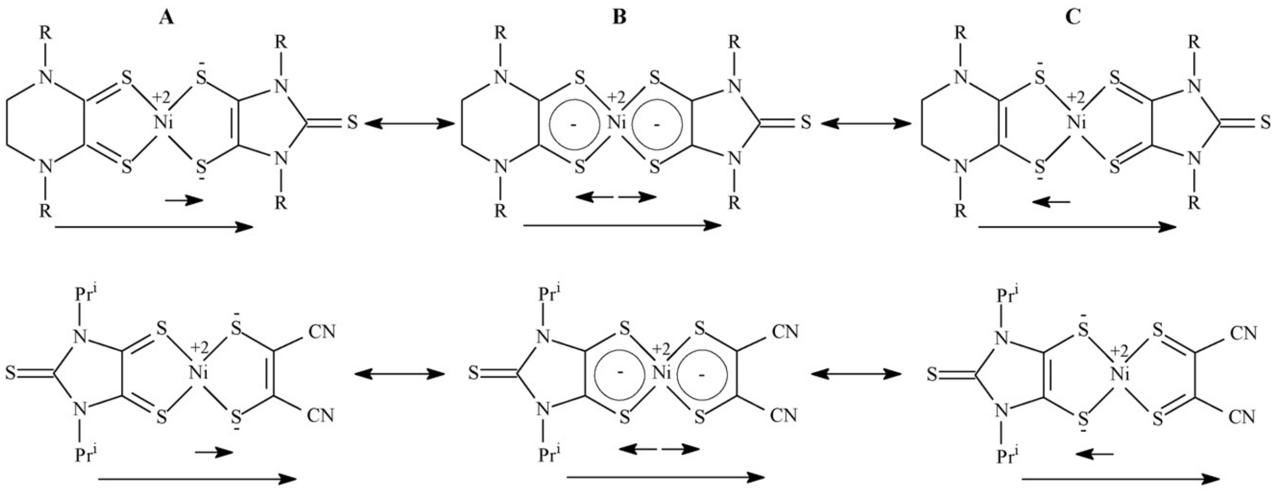
A different response is observed when the two NR groups adjacent to the $C_2S_2$ are inserted in five- rather than six-membered rings ($R_2$timdt vs $R_2$pipdt), and an almost null $\beta_0$ value has been measured for the complex [Ni($Pr^i{}_2$timdt)(mnt)], although the absence of NLO properties is accompanied by a large dipole moment in the ground state (experimental $\mu_g$ value = 16 D).

A different response between two mixed-ligand complexes has been also observed by comparing the [Ni[$(EH)_2$pipdt](tfd)] (second order NLO chromophore) and [Ni(dtmopedt)(tfd)] (no second order activity) behaviour.

A reasonable explanation for the different behaviour of asymmetrical complexes describable mainly as π-localized dithione–dithiolato [Ni($R_2$pipdt)(tdf)] (**A**) and π-delocalized [Ni(dtmopedt) (tdf)] (**B**) dithiolenes has been proposed by Chen and coworkers [21] by taking into account that the dipole moment $\mu_g$ has two components. One component arises from the periphery of the molecule (from the donor to the acceptor–substituents) the other one originates from the metal to the dithiolato-sulfurs, when the resonance form **A** is prevailing in the ground state. While the first component will remain essentially unchanged, the second one will change upon excitation due to the charge-transfer transition from the dithiolate to the dithione ligand. Instead when the resonance form **B** is prevailing in the ground state with a nearly symmetrical charge distribution at the $(C_2S_2)Ni(C_2S_2)$ core, also the second component will remain almost unchanged (see Scheme 6). As cited above, in the asymmetrical dithiolenes where both complexes are coordinated to one ligand bearing a potential NR donor group but inserted in a five ($Pr^i{}_2$timdt) or six-membered ring ($R_2$pipdt) and to one-electron-withdrawing ligand (dmit, mnt) a different NLO response is observed: an almost null $\beta_0$ value accompanied by a large dipole moment relatable to the presence of the dipole arising from the periphery of the molecule for the complex [Ni($Pr^i{}_2$timdt)(mnt)], and a negative $\beta_0$ with a slightly smaller dipole moment for the complex [Ni($Pr^i{}_2$pipdt)(dmit)]. Interestingly [Pd($Et_2$timdt)(mnt)], containing the same couple of ligands of [Ni($Pr^i{}_2$timdt)(mnt)] having null second order activity, shows structural, vibrational and electronic spectral features, which suggest a π-localized dithione–dithiolato structure [39] and a non-null second order activity. Further theoretical and experimental studies on varying the metal are required to better investigate these intriguing results.

Theoretical calculations have been performed on the [M($R_2$timdt)(dmit)] (Ni, Pd, Pt) triad and the obtained results allow to predict a non-null second order activity for these complexes. In particular TD-DFT calculations, taking into account scalar relativistic contributions to evaluate hyperpolarizability using the zero-order regular approximation, have shown that the second order response is higher in the presence of the platinum metal. Moreover it is pointed out that the two-state model is inadequate to fully explain the calculated trends, which suggest that other excitations involving the metal are important for the second order response [54].

Further theoretical studies based on Gaussian98 calculations at the DFT/B3LYP level on models compounds [Ni($R_2$pipdt)(dmit)/(mnt)], [Ni($R_2$timdt)(dmit)/(mnt)], where hydrogen atoms replace the alkyl groups of $R_2$pipdt and $R_2$timdt, have allowed to elucidate the different roles of the two *push* and *pull* ligands, but also the peculiar perturbation of the π-electron density induced by the terminal $CS_3$ grouping of the ligand dmit, which induces major differences between the ground and excited states. Similarly to symmetric complexes the HOMOs and the LUMOs of the models are still ***i.p.*** and ***o.o.p.*** combinations of the critical $C_2S_2$ frontier π-orbital but the atomic contributions are



**Scheme 6.**

**Table 6**
Summary of structure/properties relationship in square-planar $d^8$ metal mixed-ligand dithiolene complexes.

| | | |
|---|---|---|
| |  | |
| Prevailing resonance form in the ground state | π-Delocalized<br>Similar *push*/*pull* character of the ligands | π-Localized<br>Different *push* (R)/*pull* (R′) character of the ligands |
| Predictable optical properties | Electrochromic NIR dyes | Second Order NLO chromophores |
| *Suitable markers* | | |
| $\lambda_{max}$ | Vis–NIR[a] | Vis–NIR[a] |
| $\varepsilon$ | High | Medium to low |
| (C=C) distance | Similar in the two ligands | Longer (R, *push* ligand) and shorter (R′, *pull* ligand) |
| $\nu$(C=C) typical of | Dithiolenes | Dithiolate |
| Reduction potentials dependent on | Both ligands | *Push* ligand |

[a] $\lambda_{max}$ at higher wavelengths for π-delocalized system with respect to π-localized one if two complexes bearing the same *pull* ligand are compared (see Table 3).

now unbalanced, particularly when the ligand $H_2$pipdt is present. This ligand has greater weight in the LUMO. Another important aspect is the scarce contribution of the terminal $CS_3$ moiety of dmit to the LUMO of both complexes [Ni($H_2$pipdt)/($H_2$timdt)(dmit)], as shown in Fig. 6 for [Ni($H_2$pipdt)(dmit)]. Thus while the $p_\pi$-orbital populations change more at the core than at the peripheral atoms, the terminal S-atom of the dmit ligand is significantly less populated in the excited state. Therefore also the dipole component arising from the periphery of the molecule will change upon excitation. This is in agreement with non-zero NLO properties predicted for the complexes [M($H_2$timdt)(dmit)], despite they exhibit the lower charge-separated character and highest delocalization, almost comparable with the symmetric analogues, in the ground state. The unique role of dmit ligand in perturbing the electron distribution at the dithiolene core and in inducing major differences between the ground and excited states explains the peculiarity of mixed-ligand complexes based on dmit. This shows that the simplification to take constant the variation of the dipolar component arising from the periphery of the molecule upon excitation is not generally applicable, and that mixed-ligand complexes based on dmit seem optimal candidates to induce second order NLO properties at molecular level.

## 3. Conclusions and perspectives

The features of $d^8$ metal mixed-ligand dithiolene complexes suggest they can have an important role to play in the field of NLO materials. The improved understanding of structure/properties relationship and knowledge of the factors which govern the π-electron distribution in these complexes will allow chemists to tailor species with predictable optical properties. Depending on the differences in the *push*/*pull* character of the two ligands, mixed-ligand complexes exhibit an asymmetric distribution of the charge at the [($C_2S_2$)M($C_2S_2$)] core. Where a significant difference in the *push*/*pull* character occurs (π-localized system, reflected by structural data, spectroscopic and electrochemical features), the *pull* ligand (dithiolate) contributes mostly to the HOMO, the *push* ligand (dithione) mostly to the LUMO, and the HOMO–LUMO transition will have ligand-to-ligand charge-transfer (CT) character. This transition will give rise to a peak falling in the visible region and will show negative solvatochromism and value of $\beta$. Methods (6a) and (6b) (Section 2.1) being based on symmetrical complexes accessible in different redox status, having different *push*/*pull* character of the ligands, are suitable to prepare mixed-ligand derivatives to be used as second order NLO chromophores.

Where, although asymmetric, the complexes have comparable *push*/*pull* capability of the two different ligands, they compare better with the symmetric analogues for which an overall π-delocalized system is most appropriate to describe the ground state. These mixed-ligand complexes will not have second order nonlinear activity but will be suitable as NIR dyes. Methods (4a)–(4c) (Section 2.1) which use symmetrical complexes accessible in the same status, having similar *push*/*pull* character of the ligands, are most appropriate to prepare mixed-ligand complexes suitable as NIR dyes.

Structural data, spectroscopic and electrochemical features reflect the delocalized/localized π-electron distribution, and suitable markers such as $\lambda_{max}$, $\varepsilon$, $\nu$(C=C); reduction potentials work well to distinguish the limiting forms to predict the optical properties (Table 6).

Analogies with the features exhibited by the $d^8$ metal diimino–dithiolate complexes, which in addition to their NLO properties, have shown interesting properties as luminescent materials (Pt-derivatives) [22a] or as sensitizers for photogeneration of $H_2$ from water with a system based on $TiO_2$ [25] or as dyes for solar cells, [26] stimulate interest to exploit similar research lines.

Several aspects need to be further investigated, and first of all detailed photophysical studies on a systematic variation of the ligands and the metals are required.

This systematic study will allow to collect NLO data on the molecules and bulk materials of well characterized samples for the formation of a database useful to compare experimental with theoretical results with a view to relating the second order nonlinear properties with the charge-separated character of the complexes and to find a reliable structure/property relationship. Future work can be addressed to investigate the redox-induced switching of the first hyperpolarizability of these redox-active complexes. Methods for modulating molecular NLO responses are currently attracting great interest, and relevant results based mostly on ruthenium complexes have appeared recently in the literature [55].

Additional properties of the complexes, such as optical transparency, NLO response time, processability are required for their possible use in optical devices. In particular Variation of groups at the periphery of the ligands is expected to improve solubility; to introduce functional groups to favour the processing of the products in form of thin films, or sol gel glasses, or also anchoring to $TiO_2$ surfaces; or to affect the solid-state properties of the complexes. This is important both with the view to obtain crystals in a non-centrosymmetric space group which is crucial in order to maintain second order NLO activity in the bulk, and also to promote π-stacking which can affect the electroconductive properties of the complexes.

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