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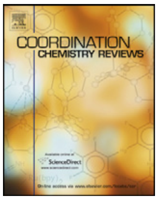

Review

Radical CpNi(dithiolene) and CpNi(diselenolene) complexes: Synthetic routes and molecular properties

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ABSTRACT

The formally Ni(III) d^7 radical organometallic complexes formulated as $[\mathrm{CpNi(dithiolene)}]^\bullet$ can be prepared by different routes involving different CpNi sources such as the $\mathrm{Ni^{(I)}}$ $[\mathrm{CpNi(CO)}]_2$, the $\mathrm{Ni^{(II)}}$ $[\mathrm{Cp_2Ni}]$ or $[\mathrm{CpNi(cod)}]^+$ or the $\mathrm{Ni^{(III)}}$ $[\mathrm{Cp_2Ni}]^+$ complexes. As dithiolene precursors, the naked dithiolate, the mono- as well as bis-(dithiolene) metal complexes were investigated. The highest yields are generally associated with an appropriate redox match, that is a $\mathrm{CpNi^{(II)}}$ precursor with a formally $\mathrm{Ni^{(IV)}}$ $[\mathrm{Ni(dithiolene)_2}]^0$ complex, or a $\mathrm{CpNi^{(III)}}$ precursor with a formally $\mathrm{Ni^{(III)}}$ $[\mathrm{Ni(dithiolene)_2}]^-$ complex. The structural, electrochemical and spectroscopic (UV–vis–NIR, EPR) properties of more than twenty complexes are described and compared, with the help of DFT calculations. They all exhibit a small optical gap with a low-energy absorption band in the Near Infra-Red region, between 700 and 1000 nm. The smaller electrochemical and optical gap found in the [CpNi(dmit)] and [CpNi(dddt)] complexes is correlated with an extensive delocalisation of the spin density in these complexes, while the other members of the series are characterized with a larger and sizeable spin density on the cyclopentadienyl ring.

1. Introduction

Homoleptic dithiolene complexes, and particularly the square-planar bis(dithiolene) ones, have been intensively investigated in material science, as precursors of molecular conductors [1], as semiconductors for field-effect transistors [2], as NIR dyes for lasers [3,4], liquid crystal devices [5], optical recording disks [6], non-linear optical devices (NLO) [7], probable olefin purification system [8]... Besides this extended class of compounds,

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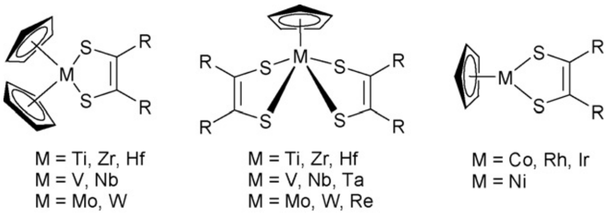
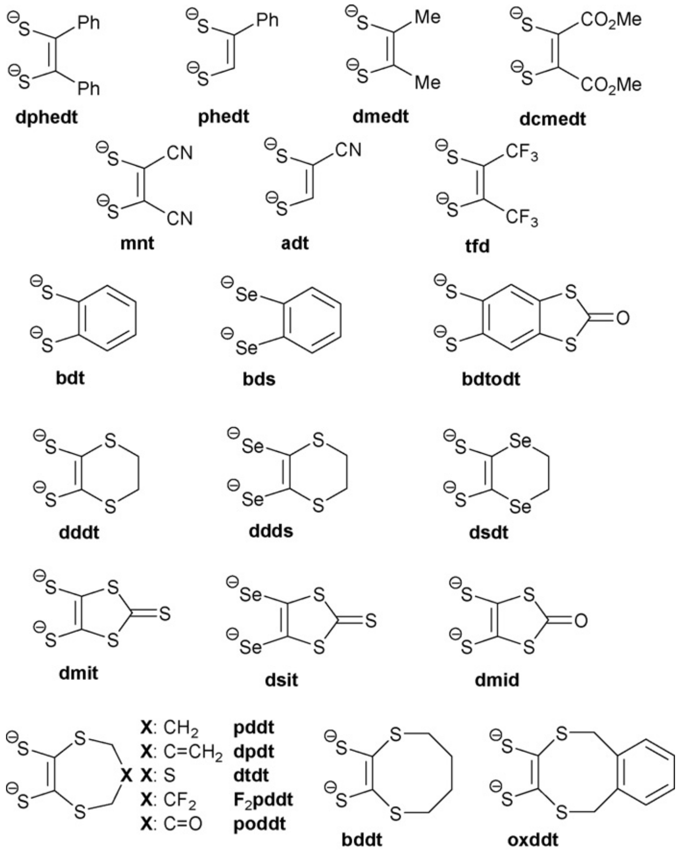


Scheme 1. Different classes of heteroleptic Cp/dithiolene complexes.

heteroleptic dithiolene complexes which associate one (or several) dithiolate ligand(s) with other ligands (cyclopentadienyl, ortho-diimines, diphosphines...) offer also a variety of complexes with multiple applications, such as models of enzymes [9], luminescent properties [10], photo- [11], thermo- [12], solvatochromism [13], photo catalyst for molecular hydrogen production [14], or dye-sensitised solar cell [15]. Dithiolene complexes involving η^5-cyclopentadienyl (Cp) [16], η^6-arene (C_6R_6) [17], or η^4-cyclobutadiene (C_4R_4) [18] ligands are also an interesting category of organometallic dithiolene complexes. Among them, the Cp/dithiolene complexes have been much more investigated compared with others. The Cp derivatives have been described in essentially three classes (Scheme 1) [16]; Cp_2M(dithiolene) and CpM(dithiolene)$_2$ complexes are known with the early transition metals (groups 4–6) while the 1:1 CpM(dithiolene) complexes are described with group 9 and 10 metal atoms (Co, Rh, Ir and Ni).

Among these complexes, the *paramagnetic* species such as the formally d^1 [Cp_2Mo(dithiolene)]$^{\bullet+}$ or [Cp*Mo(dithiolene)$_2$]$^\bullet$ complexes or the formally d^7 [CpNi(dithiolene)]$^\bullet$ have been specifically investigated as they offer a wide variety of magnetic structures in the solid state. The d^1 complexes are characterized by strong distortions of the MS_2C_2 metallacycles and a large delocalisation of the spin density between the metal and the dithiolene ligands [19,20]. Besides, the formally d^7 [CpNi(dithiolene)]$^\bullet$ radical complexes are rigid, stable in aerial conditions and most often well crystalline. In a formal electron count, they can be written either as Ni(II) species with an oxidized $(R_2C_2S_2)^{\bullet-}$ dithiolate radical anion ligand, or as a Ni(III) species coordinated to the dithiolate $(R_2C_2S_2)^{2-}$ ligand. They are characterized by a spin density delocalised not only on the nickel and dithiolene moieties but also on the Cp ring, an attractive feature which allows for the setting of strong antiferromagnetic interactions in the solid state through face-to-face Cp···Cp overlap [21]. While the solid state structural and magnetic properties of these classes of heteroleptic dithiolene compounds have been recently reviewed [19–21], a comprehensive review of their syntheses and molecular properties was not available and is the object of the present work.

Indeed, over the past years, many different experimental routes have been described to optimize their preparation, involving different sources of the CpNi moiety, in a Ni(I), Ni(II) or Ni(III) oxidation state. Similarly, a variety of dithiolate precursors, eventually partially oxidized, has been also used to react with the CpNi moiety. In this paper, we have gathered the different synthetic methods explored so far for the preparation of the [CpNi(dithiolene)] complexes, with the hope that some guidelines will come out to choose the most efficient method for a given dithiolate ligand. In Section 2, these methods have been classified according to the nature of the dithiolate derivative used for the synthesis. In Section 3, a thorough comparison of available electrochemical data on these radical complexes allowed us to identify various trends in these series, in relation with the Near Infra-Red (NIR) absorption band these complexes exhibit, from 700 to 1000 nm. This will be complemented by exhaustive structural and magnetic data. More than twenty dithiolate ligands have been used so far to prepare the corresponding [CpNi(dithiolene)]$^\bullet$ complexes. They are detailed in Scheme 2 together with their acronyms and full formulae.

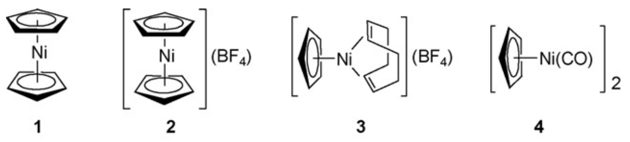


Scheme 2. Chemical structures of dithiolate ligands. dphedt = 1,2-diphenylethylene-1,2-dithiolate, phedt = phenylethylene-1,2-dithiolate, dmedt = 1,2-dimethylethylene-1,2-dithiolate, dcmedt = 1,2-dimethoxycarbonylethylene-1,2-dithiolate, tfd = 1,2-bis(trifluoromethyl)ethylene-1,2-dithiolate, mnt = maleonitrile-1,2-dithiolate, adt = acrylonitrile-2,3-dithiolate, bdt = benzene-1,2-dithiolate, bds = benzene-1,2-diselenolate, bdtodt = benzo[1,3]dithiol-2-one-5,6-dithiolate, dddt = 5,6-dihydro-1,4-dithiin-2,3-dithiolate, ddds = 5,6-dihydro-1,4-dithiin-2,3-diselenolate, dsdt = 5,6-dihydro-1,4-diselenin-2,3-dithiolate, dmit = 1,3-dithiol-2-thione-4,5-dithiolate, dmid = 1,3-dithiol-2-one-4,5-dithiolate, dsit = 1,3-dithiol-2-thione-4,5-diselenolate, pddt = 6,7-dihydro-5*H*-1,4-dithiepin-2,3-dithiolate, dpdt = 6,7-dihydro-6-methylene-5*H*-1,4-dithiepine-2,3-dithiolate, dtdt = 5,7-dihydro-1,4,6-trithiin-2,3-dithiolate, F_2pddt = 6,6-difluoro-6,7-dihydro-5*H*-1,4-dithiepine-2,3-dithiolate, poddt = 5*H*-1,4-dithiepin-6(7*H*)-one-2,3-dithiolate, bddt = 5,6,7,8-tetrahydro-1,4-dithiocine-2,3-dithiolate, oxddt = *o*-xylenediyldithioethylene-1,2-dithiolate.

2. Preparations of CpNi(dithiolene) and CpNi(diselenolene) complexes

2.1. Different sources of the CpNi moiety

All CpNi sources described in this paper are shown in Scheme 3: nickelocene, [Cp_2Ni] (**1**) (Cp = η^5-cyclopentadienyl), nickelocenium, [Cp_2Ni]$^+$ (**2**), as its tetrafluoroborate salt, [CpNi(cod)]$^+$ (**3**) as tetrafluoroborate salt (cod = 1,5-cyclooctadiene), and η^5-cyclopentadienyl nickel carbonyl dimer, [CpNi(CO)]$_2$ (**4**). **1** and **2** are metallocene complexes with 20e$^-$ and 19e$^-$ electrons, respectively. Such electron-rich (more than 18e$^-$) species are easy to convert to the corresponding half-metallocene complexes, fol-



Scheme 3.

Table 1
Reactions of CpNi sources with some naked 1,2-dithiolates (see Scheme 4).

Entry	Dithiolate	CpNi source	Molar ratio	Solvent	Temp.	Time (h)	Product	Yield (%)	Ref.
1	dddt	**1**	1:1	MeOH	rt	0.5	[CpNi(dddt)]	6.5	[26]
2	dddt	**2**	1:1	MeOH	rt	0.5	[CpNi(dddt)]	28	[26]
3	dddt	**3**	1:1	MeOH	rt	0.5	[CpNi(dddt)]	17	[26]
4	mnt	**1**	1:1	MeOH	Reflux	2	[CpNi(mnt)]	2.5	[27]
5	mnt	**2**	1:1	MeOH	Reflux	2	[CpNi(mnt)]	2.7	[27]
6	mnt	**3**	1:1	MeOH	Reflux	2	[CpNi(mnt)]	2.3	[27]

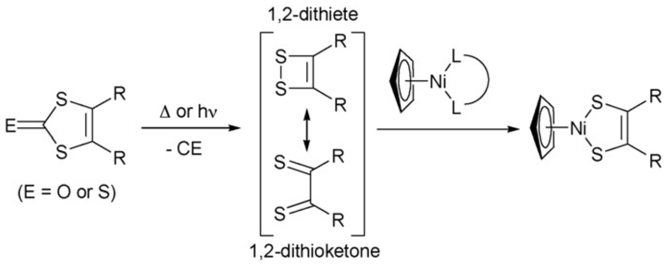
lowing Cp ligand elimination [22]. On the other hand, **3** and **4** are already half-metallocene complexes, and the cod and CO ligands are useful for ligand exchange reactions [22,23]. All reported syntheses of the formally Ni(III) CpNi(dithiolene) complexes will involve these CpNi sources **1**–**4** and dithiolene transfer sources, together with an appropriate redox match between both partners. Indeed, the formers can be either the Ni(I) source (**4**), the Ni(II) sources (**1** and **3**) or the Ni(III) source (**2**). Dithiolene sources can be a naked 1,2-dithiolate(2−), a protected 1,2-dithiolate(2−), a naked 1,2-dithiete(0) (or 1,2-dithioketone(0)), a protected 1,2-dithioketone(0), and a protected 1,2-dithiosemiquinone(1−).

2.2. *Reactions involving naked 1,2-dithiolates*

Metal dithiolene complexes can be prepared by metathesis reaction from metal halides and naked 1,2-dithiolates $(R_2C_2S_2)^{2-}$ [24]. The reactions of the CpNi sources **1**–**3** with the naked dddt^{2-} or mnt^{2-} ligands (Scheme 4) are summarized in Table 1. The dddt^{2-} was prepared by the treatment of O=C(dddt) with sodium methoxide (2 equiv.) and was not isolated. Successive additions of **1**–**3** into the reaction mixture formed [CpNi(dddt)] in 6–28% isolated yields (entries 1–3 in Table 1). The initial product in this reaction may be the monoanionic [CpNi(dddt)]$^-$ (obtained as a brown solution in MeOH). When the reaction mixture was treated under aerobic conditions, the expected greenish-brown solution was obtained. However, before the addition of **1**–**3**, the reaction to generate dddt^{2-} should be performed under inert gas atmosphere, since the naked dddt^{2-} is air-sensitive. These reactions are performed at room temperature for 30 min after the additions of **1**–**3**, while reaction at higher temperatures or for longer reaction time caused a decomposition of the product. We assume that the monoanionic product [CpNi(dddt)]$^-$ may be thermodynamically not stable enough or simply not stable under basic conditions. The mnt^{2-} dianion is isolable and commercially available as a disodium salt. Many dithiolene complexes of mnt^{2-} have been prepared so far from the reaction with metal salts [25]. However here, the attempted reactions of **1**–**3** with Na$_2$(mnt) gave [CpNi(mnt)] only in very low yields (entries 4–6 in Table 1). As shown in Table 1, this metathesis reaction path does not appear to provide satisfactory yields, be it with electron-rich (dddt^{2-}) or electron-poor (mnt^{2-}) dithiolate ligands.

2.3. *Reactions involving 1,3-dithiol-2-one and 1,3-dithiol-2-thione derivatives*

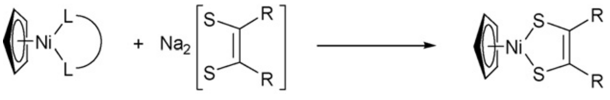
1,3-Dithiol-2-one (O=C($S_2C_2R_2$)) and 1,3-dithiol-2-thione (S=C($S_2C_2R_2$)) derivatives are also well-known as good precursors for metal dithiolene complexes. The dithiocarbonate can generate, under thermal or photochemical (UV) conditions and carbon monoxide elimination, the 2e$^-$ oxidized species of the 1,2-dithiolate dianion, that is the neutral 1,2-dithiete(0) or 1,2-dithioketone(0) intermediates, sometimes in equilibrium (Scheme 5) [28]. When the R groups are electron-withdrawing substituents, the 1,2-dithiete form is more stable than the other [29]. When the R groups are bulky (R = *t*-butyl or 1-adamantyl), the equilibrium between both species has been identified [29]. The molecular structure of 3,4-bis(1-adamantyl)-1,2-dithiete has been reported by Holm and co-workers [30]. Anyway, the 1,2-dithiete and 1,2-dithioketone forms show the same reactivities with low-valent metal sources, and then dithiolene complexes of higher valent metal can be obtained [24]. Accordingly, low-valent CpNi(I) and CpNi(II) sources should be good precursors for the preparation of CpNi(III)(dithiolene) complexes, since both 1,2-dithiete and 1,2-dithioketone forms are oxidizing molecules.



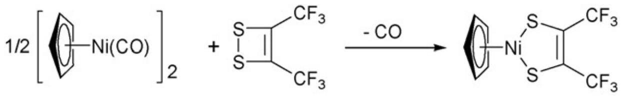
Scheme 5.

Indeed, the very first [CpNi(dithiolene)] complex ever prepared, [CpNi(tfd)], was reported already in 1963 by King, who obtained it from the reaction of **4** with 1,2-bis(trifluoromethyl)dithiete in 48% yield (Scheme 6) [31]. However, most 1,2-dithietes or 1,2-dithioketones are hard to isolate [28,29]. Accordingly, the *in situ* generation of those species from 1,3-dithiol-2-one or 1,3-dithiol-2-thione derivatives has been investigated, followed by the reaction with **1** or **4** to prepare [CpNi(dithiolene)] complexes (Scheme 5). Thermal reactions were performed at 80–110 °C, and photochemical reactions were carried out under UV irradiation in degassed solution at room temperature. These results are summarized in Table 2.

In the thermal reaction, both 1,3-dithiol-2-one (Scheme 5, E = O) and 1,3-dithiol-2-thione (Scheme 5, E = S) derivatives could be used for the preparation of [CpNi(dcmedt)], but a higher temperature was required for the activation of the thiocarbonyl group of the 1,3-dithiol-2-thione (entries 7 *vs.* 8 in Table 2). Most 1,3-dithiol-2-thione derivatives are easily transformed into the corresponding 1,3-dithiol-2-one in quantitative yield from reaction with Hg(OAc)$_2$, and these 1,3-dithiol-2-one derivatives proved to be more reactive. For example, King's complex [CpNi(tfd)] could be obtained, albeit in low yield, from **4** and O=C(tfd) under heating



Scheme 4.



Scheme 6.

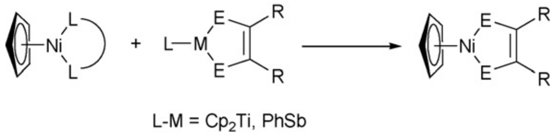
Table 2
Reactions of CpNi sources with 1,3-dithiol-2-one (E = O) and 1,3-dithiol-2-thione (E = S) under thermal or photochemical conditions (see Scheme 5).

Entry	E		CpNi source	Molar ratio	Solvent	Condition	Time (h)	Product	Yield (%)	Ref.
7	O	dcmedt	**1**	1:1	Benzene	$h\nu$	4	[CpNi(dcmedt)]	31	[33]
8	S	dcmedt	**1**	1:1	Xylene	Reflux	0.5	[CpNi(dcmedt)]	16	[33]
9	O	tfd	**4**	2:1	Toluene	80 °C	2	[CpNi(tfd)]	5.9	[34]
10	O	phedt	**1**	1:1	Benzene	$h\nu$	12	[CpNi(phedt)]	32	[33]
11	O	dddt	**1**	1:1	Toluene	Reflux	24	[CpNi(dddt)]	29	[26]
12	O	dddt	**1**	1:1	Toluene	$h\nu$	24	[CpNi(dddt)]	30	[26]
13	O	dddt	**4**	2:1	Toluene	Reflux	6	[CpNi(dddt)]	29	[26]
14	O	dddt	**4**	2:1	Toluene	$h\nu$	24	[CpNi(dddt)]	15	[26]
15	O	poddt	**1**	1:1	Toluene	Reflux	24	[CpNi(poddt)]	9	[35]
16	O	poddt	**1**	1:1	Toluene	$h\nu$	24	[CpNi(poddt)]	9	[35]
17	O	poddt	**4**	2:1	Toluene	Reflux	6	[CpNi(poddt)]	15	[35]
18	O	bdtodt	**1**	1:10	Toluene	Reflux	24	[CpNi(bdtodt)]	26	[36]

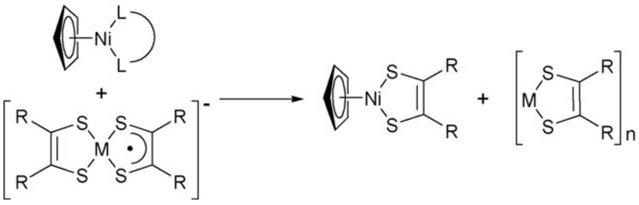
(entry 9 in Table 2) without using 1,2-bis(trifluoromethyl)dithiete [31]. Thermal and photoreactions of **1** with O=C(dddt) gave [CpNi(dddt)] in ≈30% yield (entries 11 and 12 in Table 2). Note also that the reaction of O=C(dddt) with 1/2 equiv. of $[\text{CpNi(CO)}]_2$ (**4**) or with one equiv. of $[\text{Cp}_2\text{Ni}]$ (**1**) gave similar yields, and a faster reaction with **4** (entries 13 and 14 in Table 2). One possible reason is that the CO ligand in **4** is efficiently eliminated to generate a reactive CpNi intermediate under the thermal conditions or photo-irradiation [23]. However, as shown in Table 2, the best yield for these thermal of photochemical activation reactions do not exceed 32%. Another most important point is also the requirement for a good solubility of the dithiolene precursors. For example, [CpNi(poddt)] has been obtained only by this route, reacting the corresponding dithiocarbonate O=C(poddt) with **1** or **4**, while other poddt precursors were too insoluble to react. The reaction of the benzene 1,2,4,5-tetrathiolate precursor, that is benzo[1,2-d;4,5-]bis[1,3]dithiole-2,6-dione [32], with **1** afforded only the monometallic complex [CpNi(bdtodt)] in 26% yield, while the corresponding bimetallic derivative, that is $[\text{CpNi(C}_6\text{H}_2\text{S}_4\text{)NiCp}]$, was not observed, even in the presence of an excess of **1** was used (entry 18 in Table 2).

2.4. Reactions involving mono(dithiolene) complexes

Some metal dithiolene complexes themselves can be good precursors for other metal dithiolene complexes (transmetalation) and dithiolene transfer reactions to other transition metals have been previously reported [24]. For example, titanium, tin, antimony and zinc dithiolene complexes such as $[\text{Cp}_2\text{Ti(dithiolene)}]$ [37], $[\text{Bu}_2\text{Sn(dithiolene)}]$ [38], [PhSb(dithiolene)] [39] or $(\text{NR}_4)_2[\text{Zn(dithiolene)}_2]$ [40] have been reported for that purpose. In these complexes, the dithiolene ligand is present as 1,2-dithiolate(2−) form. The reactions of Cp_2Ti and PhSb dithiolene (or diselenolene) complexes with **1**–**3** (Scheme 7) are summarized in Table 3. We also report here the unpublished reaction of $[\text{Cp}_2\text{Ti(diselenolene)}]$ complexes, which was investigated in the search for an efficient preparation of [CpNi(diselenolene)] marked with ^{77}Se [41]. The reactions of $(\text{NR}_4)_2[\text{Zn(dithiolene)}_2]$ (or diselenolene) are described in Part 2.7. $[\text{Cp}_2\text{Ti(bds)}]$ reacted with **2** or **3** to form [CpNi(bds)] in 13% or 26% yield, respectively (entries 20 and 21 in Table 3). However, no reaction was found between $[\text{Cp}_2\text{Ti(bds)}]$ and **1** (entry 19 in Table 3). The reactions of [PhSb(dithiolene)] series with **2** gave [CpNi(dmit)], [CpNi(dmid)] and [CpNi(dsit)] in 26%, 6%, and 36% yields, respectively (entries 22–24).



Scheme 7.



Scheme 8.

2.5. Reactions involving monoanionic bis(dithiolene) Ni and Pd complexes

Faulmann et al. have reported the first synthesis of [CpNi(dmit)], obtained by serendipity from the reaction of **2** and $\text{Na[Ni(dmit)}_2]$ in 28% yield in acetone/MeOH solution [43], in their attempts to prepare the complex salt $[\text{Cp}_2\text{Ni}]^+[\text{Ni(dmit)}_2]^-$. We found that the reaction yield was improved up to 47% when using the Bu_4N^+ salt of $[\text{Ni(dmit)}_2]^-$ (entry 25 in Table 4). Similar reactions were observed to form [CpNi(dmid)] (12% yield), [CpNi(mnt)] (68% yield), [CpNi(adt)] (32% yield), and [CpNi(dcmedt)] (67% yield) from the corresponding monoanionic $[\text{Ni(dithiolene)}_2]^-$ complexes and **2** (entries 26–29 in Table 4). All reactions should be performed in a polar solvent (e.g. MeCN, MeOH), because of the ionic nature of the reactants in these reactions (Scheme 8).

Table 3
Reactions of CpNi sources with LM(dithiolene) or LM(diselenolene) complexes (see Scheme 7).

Entry	L–M	Dithiolene/diselenolene	CpNi source	Molar ratio	Solvent	Temp.	Time (h)	Product	Yield (%)	Ref.
19	Cp_2Ti	bds	**1**	1:1	Toluene	80 °C	2	–	NR	[27]
20		bds	**2**	1:1	MeOH	Reflux	2	[CpNi(bds)]	13	[27]
21		bds	**3**	1:1	MeOH	Reflux	2	[CpNi(bds)]	17	[27]
22	PhSb	dmit	**2**	1:1	MeCN/THF	rt	18	[CpNi(dmit)]	26	[42]
23		dmid	**2**	1:1	MeCN/THF	rt	2	[CpNi(dmid)]	6	[42]
24		dsit	**2**	1:1	MeCN/THF	rt	2	[CpNi(dsit)]	36	[42]

Table 4
Reactions of CpNi sources with monoanionic bis(dithiolene) complexes $[M(dithiolene)_2]^-$ (see Scheme 8). $E_{1/2}$(ox) gives the half-wave redox potential (*vs.* Fc/Fc^+) for the corresponding $[M(dithiolene)_2]^-/[M(dithiolene)_2]$ couple, to be compared with the $[Cp_2Ni]/[Cp_2Ni]^+$ redox process observed at −0.42 V *vs.* Fc/Fc^+.

Entry	M		CpNi source	Molar ratio	$E_{1/2}$(ox)/V (−1/0)	Solvent	Temp.	Time (h)	Product	Yield (%)	Ref.
25	Ni[a]	dmit	**2**	1:1	−0.19	MeCN	rt	2	[CpNi(dmit)]	47	[42]
26	Ni[a]	dmid	**2**	1:1	–[e]	MeCN	rt	3	[CpNi(dmid)]	12	[42]
27	Ni[a]	mnt	**2**	1:1	+0.69	MeOH	Reflux	1	[CpNi(mnt)]	68	[33]
28	Ni[b]	adt	**2**	1:1	+0.15	MeCN	rt	3	[CpNi(adt)]	32	[34]
29	Ni[b]	dcmedt	**2**	1:1	+0.11	MeOH	rt	2	[CpNi(dcmedt)]	67	[33]
30	Ni[a]	dphedt	**2**	1:1	−0.49	MeOH	rt	2	[CpNi(dphedt)]	29[c]	[33]
31	Ni[a]	phedt	**2**	1:1	−0.43	MeOH	rt	2	[CpNi(phedt)]	47	[33]
32	Pd[a]	dphedt	**2**	1:1	−0.39	MeOH	rt	2	[CpNi(dphedt)]	72	[33]
33	Ni[a]	dddt	**2**	1:1	−0.33	MeOH	Reflux	2	[CpNi(dddt)]	59	[26]
34	Ni	*idem*	**1**	1:1	*idem*	Toluene	80 °C	2	–[d]	0	[26]
35	Ni	*idem*	**3**	1:1	*idem*	MeOH	Reflux	2	[CpNi(dddt)]	86	[26]
36	Ni[a]	poddt	**2**	1:1	–[e]	MeOH	Reflux	2	–[d]	0	[35]
37	Ni[a]	bddt	**3**	1:1	–[e]	MeOH	Reflux	2	[CpNi(bddt)]	30	[44]

[a] Bu_4N^+ salt was used.
[b] Ph_4P^+ salt was used.
[c] The neutral complex $[Ni(dphedt)_2]^0$ was also obtained in 70% yield.
[d] No reaction.
[e] Not reported.

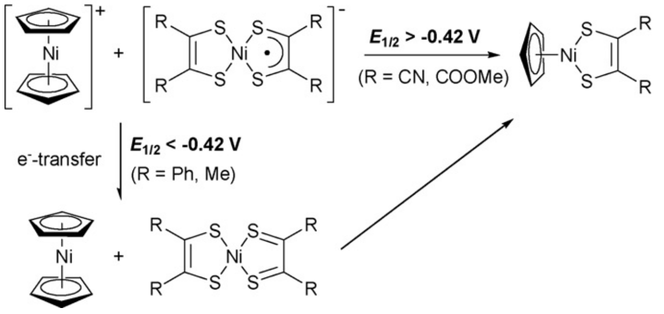
These complexes described above are substituted with electron-withdrawing groups such as CN, COOMe, CO and C=S. As a consequence, the starting $[Ni(dithiolene)_2]^-$ complexes are stable under oxidative conditions. On the other hand, the monoanionic $[Ni(dithiolene)_2]^-$ complexes bearing Ph or electron-releasing groups (Me, Ph) can be readily oxidized by nickelocenium (**2**) before any reaction takes place. This electron-transfer reaction obviously forms the neutral $[Ni(dithiolene)_2]^0$ and nickelocene (**1**) (Scheme 9), which might precipitate in the polar solvent used to dissolve the starting salts. This is probably at the origin of the poor yield obtained for the preparation of [CpNi(dphedt)] (entry 30 in Table 4) by this method.

As an element of comparison, the oxidation potentials of the starting monoanionic $[Ni(dithiolene)_2]^-$ complexes have been given in Table 4. When compared with the redox potential of $[Cp_2Ni]/[Cp_2Ni]^+$ couple ($E_{1/2} = -0.42$ V *vs.* Fc/Fc^+) [33], we observe that the monoanionic $[Ni(dmit)_2]^-$ (−0.19 V), $[Ni(dcmedt)_2]^-$ (+0.11 V), $[Ni(adt)_2]^-$ (+0.15 V) and $[Ni(mnt)_2]^-$ (+0.69 V) complexes will not suffer an electron transfer prior to chemical reaction. On the other hand, the monoanionic $[Ni(dphedt)_2]^-$ complex has a much lower oxidation potential (−0.49 V). The alternative use of the corresponding Pd complex, $[Pd(dphedt)_2]^-$ which oxidizes at a higher potential (−0.39 V) allowed for an higher reaction yield (entry 32 in Table 4), possibly attributable to the absence of electron-transfer. These results confirm that electron-rich $[Ni(dithiolene)_2]^-$ complexes can be readily oxidized by nickelocenium (**2**) before any reaction takes place.

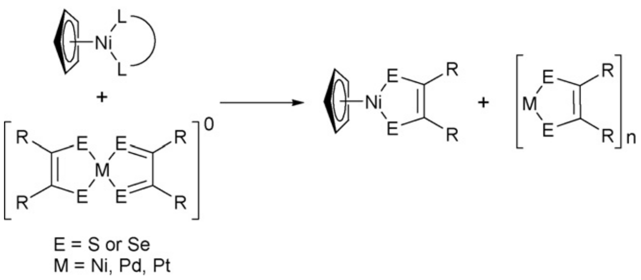
However, in the course of the reaction of $[Ni(dddt)_2]^-$ with **2**, and despite electron transfer, [CpNi(dddt)] was obtained in good yield after heating (59%, entry 33 in Table 4). In fact, this result is similar to the reaction of the neutral $[Ni(dddt)_2]^0$ with neutral nickelocene (**1**) at 80 °C in toluene as described below in Section 2.6. These results indicate that the higher temperature reaction increased the solubility of the neutral reactants formed after electron transfer. In addition, note that no reaction was indeed observed between the monoanionic $[Ni(dddt)_2]^-$ complex with **1** (entry 34). In conclusions, the highest yields of [CpNi(dithiolene)] complexes are obtained with an appropriate redox match, that is a $Cp_2Ni(II)$ species with a formally Ni(IV) $[Ni(dithiolene)_2]^0$ complex, or a $Cp_2Ni(III)$ species with a formally Ni(III) $[Ni(dithiolene)_2]^-$ complex. Note however that the reaction of $[Ni(dddt)_2]^-$ with the Ni(II) cod derivative **3** gave also [CpNi(dddt)] in very good yield (86%, entry 35), suggesting that the cod ligand of **3** is very labile when faced with dithiolene ligand. [CpNi(bddt)] was also obtained from $[Ni(bddt)_2]^-$ and **3** in 30% yield (entry 37), while other methods gave poorer yields [44].

2.6. Reactions involving neutral bis(dithiolene) Ni, Pd, and Pt complexes

As already mentioned above, the reactions of the neutral, formally Ni(IV) $[M(dithiolene)_2]^0$ (M = Ni, Pd, Pt) complexes with the Ni(II) **1** or **4** species (Scheme 10) are also very efficient for the synthesis of [CpNi(dithiolene)] complexes, as shown in Table 5. These reactions should be performed in a non-polar solvent (CH_2Cl_2, benzene and toluene) because both reactants are neutral. The neutral $[Ni(dithiolene)_2]$ complexes with soluble substituents (Ph, Me) on the dithiolene ligand react with **1** at room temperature to afford [CpNi(dphedt)], [CpNi(phedt)] and [CpNi(dmedt)] in moderate yields (50–62%, entries 38–43). On the other hand, the use of Pd and Pt complexes of dphedt resulted in lower yields (entries 44–46) than with the corresponding Ni complexes. Most



Scheme 9.



Scheme 10.

Table 5
Reactions of CpNi sources with neutral bis(dithiolene) Ni, Pd, and Pt complexes (see Scheme 10).

Entry	M	Dithiolate	CpNi source	Molar ratio	Solvent	Temp.	Time (h)	Product	Yield (%)[a]	Ref.
38	Ni	dphedt	**1**	1:1	CH_2Cl_2	rt	19	[CpNi(dphedt)]	62[a]	[33]
39	Ni	dphedt	**1**	1:1	CH_2Cl_2	Reflux	4	[CpNi(dphedt)]	50[a]	[33]
40	Ni	dphedt	**1**	1:1	Benzene	rt	3	[CpNi(dphedt)]	54[a]	[33]
41	Ni	dphedt	**1**	1:1	Benzene	Reflux	3	[CpNi(dphedt)]	56[a]	[33]
42	Ni	phedt	**1**	1:1	Benzene	Reflux	3	[CpNi(phedt)]	58	[33]
43	Ni	dmedt	**1**	1:1	CH_2Cl_2	rt	19	[CpNi(dmedt)]	58	[33]
44	Pd	dphedt	**1**	1:1	CH_2Cl_2	rt	19	[CpNi(dphedt)]	36	[33]
45	Pt	dphedt	**1**	1:1	CH_2Cl_2	rt	19	[CpNi(dphedt)]	13	[33]
46	Pt	dphedt	**1**	1:1	Toluene	Reflux	2	[CpNi(dphedt)]	32	[33]
47	Ni	dddt	**1**	1:1	Toluene	80 °C	2	[CpNi(dddt)]	62	[26]
48	Ni	dddt	**2**	1:1	Toluene	80 °C	2	–[b]	0	[26]
49	Ni	dddt	**4**	2:1	Toluene	80 °C	2	[CpNi(dddt)]	65	[26]
50	Ni	ddds	**1**	1:1	Toluene	80 °C	2	[CpNi(ddds)]	68	[26]
51	Ni	dsdt	**1**	1:1	Toluene	80 °C	2	[CpNi(dsdt)]	15	[26]
52	Ni	bdt	**1**	1:1	Toluene	80 °C	2	[CpNi(bdt)]	51[a]	[26]
53	Ni	bds	**1**	1:1	Toluene	80 °C	2	[CpNi(bds)]	40	[26]
54	Ni	pddt	**1**	1:1	Toluene	80 °C	2	[CpNi(pddt)]	54	[35]
55	Ni	F_2pddt	**1**	1:1	Toluene	80 °C	2	[CpNi(F_2pddt)]	41[a]	[35]
56	Ni	dpdt	**1**	1:1	Toluene	80 °C	2	[CpNi(dpdt)]	30	[35]
57	Ni	dtdt	**1**	1:1	Toluene	80 °C	2	[CpNi(dtdt)]	61	[35]
58	Ni	oxddt	**1**	1:1	Toluene	80 °C	2	[CpNi(oxddt)]	44	[44]

[a] Soluble monodithiolene hexamer $[M(dithiolene)]_6$ was isolated by column chromatography.
[b] No reaction.

sulfur-rich $[M(dithiolene)_2]$ complexes or benzene-fused dithiolene complexes are less soluble, but a higher reaction temperature (up to 80 °C) increased the reaction yield (entries 47, 52–58). A notable exception is [CpNi(dsdt)] (15% yield, entry 51), as the neutral $[Ni(dsdt)_2]^0$ [45] was poorly soluble in toluene even at higher temperatures. The reaction of $[Ni(ddds)_2]$, which has been formulated as a dimer in a solid state [46], with **1** produced [CpNi(ddds)] in 68% yield (entry 50). The reaction of $[Ni(dddt)_2]$ with half equiv of **4** instead of **1** afforded [CpNi(dddt)] in 65% yield (entry 49).

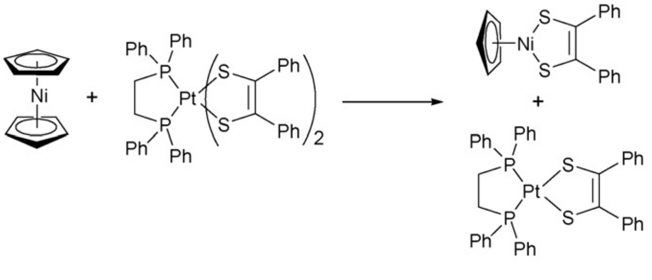
In conclusion, this reaction path is very efficient to synthesize electron-rich [CpNi(dithiolene)] complexes since the corresponding neutral $[M(dithiolene)_2]^0$ complexes are available, but provided they are soluble enough. Numerous [CpNi(dithiolene)] and [CpNi(diselenolene)] complexes have been obtained in good yields, with the added advantage that nickelocene itself (**1**) is commercially available. On the other hand, for electron-poor [CpNi(dithiolene)] complexes, the ionic reactions described in Section 2.5 (Scheme 8) are preferred since the corresponding neutral $[M(dithiolene)_2]^0$ complexes are not available (dithiolene = mnt, adt, dcmedt). For example, the neutral $[M(mnt)_2]^0$ complexes (M = Ni, Pd, Pt) can be electrochemically generated from the monoanionic species, but are not stable unless those solutions are diluted [47].

The reactions of the Pd and Pt $[M(dithiolene)_2]^0$ complexes with **1** gave only nickel-containing [CpNi(dithiolene)] complexes, without any CpPd nor CpPt complex (entries 44–46). These results indicate that the neutral $[M(dithiolene)_2]$, M = Pd, Pt, only act as dithiolene transfer agent. Similarly, the central nickel atom of $[Ni(dithiolene)_2]$ complexes is not involved in the formation of [CpNi(dithiolene)] complexes. Actually, known mono(dithiolene) oligomers [26,33,35], which are formulated as $[Ni(dithiolene)]_n$ (n = 6 by TOF mass), were isolated when soluble (Scheme 10, e.g. dithiolene = dphedt, bdt, F_2pddt). The oligomer $[Ni(dphedt)]_n$ was also obtained in the reaction of **2** with $[Ni(dphedt)_2]^-$ (Scheme 8). Formally here, the neutral $[M(dithiolene)_2]^0$ complexes (M = Ni, Pd, Pt) could be as a stable "1,2-dithiolate(2−)" and a reactive "1,2-dithioketone(0)" resonance structures. The reactive 1,2-dithioketone moiety would react with **1** or **4**, while the remaining [M(dithiolate)] fragment can be oligomerized (Scheme 10). Schrauzer, Holm et al. have also obtained the monodithiolene oligomer as a byproduct, from dithiolene transfer reactions between $[Ni(dithiolene)_2]^0$ and molybdenum and tungsten complexes [48]. As shown in Section 2.3, a naked 1,2-dithioketone (or 1,2-dithiete) can be generated by thermal or photoreaction of 1,3-dithiol-2-one derivatives, but this reaction path afforded the desired [CpNi(dithiolene)] complexes in much lower yields (Table 2). Thus, the neutral $[M(dithiolene)_2]^0$ complex appears here as an efficient, protected 1,2-dithioketone source. Similarly, the monoanionic $[Ni(dithiolene)_2]^-$ complexes appear as protected 1,2-dithiosemiquinone source, reacting preferentially with the oxidized $Cp_2Ni(III)$ (**2**) species. This analysis is further supported by the observation that no reaction occurs between two oxidized complexes such as neutral $[Ni(dithiolene)_2]^0$ and nickelocenium (**2**) (entry 48 in Table 5).

The six-coordinated $[(dppe)Pt(dphedt)_2]$ complex (dppe = 1,2-diphenylphosphinoethane) [49] can be also viewed as a hidden 1,2-dithioketone(0) precursor. Its reaction with **1** (Scheme 11) afforded [CpNi(dphedt)], in almost quantitative yield (96%), while $[Pt(dphedt)_2]$ itself showed a poor reactivity with **1** (Table 5, entries 45–46). We assume here that the dppe ligand activates the six-coordinated complex to easily eliminate the reactive '1,2-dithioketone' ligand for reaction with **1**. Actually, the four-coordinate [(dppe)Pt(dphedt)] complex was also obtained as a byproduct, following the elimination of the 1,2-dithioketone ligand [33].

2.7. Reactions involving dianionic bis(dithiolene) Zn complexes

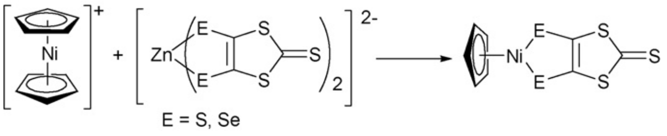
The reactions of $[Zn(dithiolene)_2]^{2-}$ with **1**–**3** (Scheme 12) are summarized in Table 6. They have not been published but we describe them here for the sake of completeness, as they were



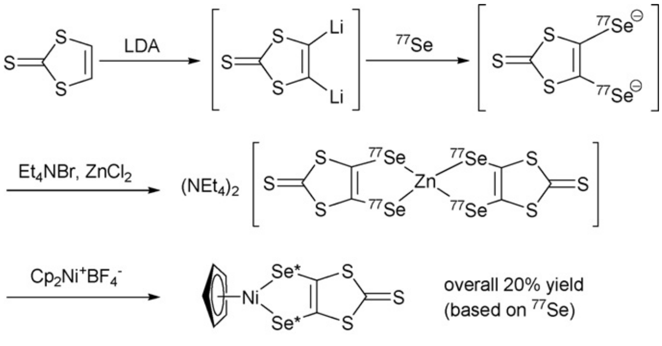
Scheme 11.

Table 6
Reactions of CpNi sources with $[Zn(dithiolene)_2]^{2-}$ or $[Zn(diselenolene)_2]^{2-}$ complexes (related to Scheme 12).

Entry	Dithiolate	CpNi source	Molar ratio	Solvent	Temp.	Time (h)	Product	Yield (%)	Ref.
59	dmit	**2**	1:2	MeOH	Reflux	2	[CpNi(dmit)]	70	[27]
60	dmit	**1**	1:2	MeOH	Reflux	2	[CpNi(dmit)]	11	[27]
61	dmit	**3**	1:2	MeOH	Reflux	2	[CpNi(dmit)]	17	[27]
62	dsit	**2**	1:2	MeOH	Reflux	2	[CpNi(dsit)]	56	[27,41]
63	dsit	**1**	1:2	MeOH	Reflux	2	[CpNi(dsit)]	5.9	[27]
64	dsit	**3**	1:2	MeOH	Reflux	2	[CpNi(dsit)]	35	[27]



Scheme 12.



Scheme 13.

originally optimized for the preparation of analogous diselenolene complexes [41]. Both dithiolene ligands in $[Zn(dithiolene)_2]^{2-}$ are formally in a '1,2-dithiolate' form, while one of two dithiolene ligands of $[Ni(dithiolene)_2]^0$ is formally in a '1,2-dithioketone' form. Interestingly, the $[Zn(dmit)_2]^{2-}$ complex reacted with 2 equiv of **2** to produce [CpNi(dmit)] in 70% yield (entry 59). This result indicates that both 1,2-dithiolate ligands in $[Zn(dmit)_2]^{2-}$ can be transferred to the CpNi fragment, while one '1,2-dithiolate' ligand in $[Ni(dithiolene)_2]$ was shown to be inactive. Polar solvents should be preferred here, because of the ionic nature of the reactants. Note also that the reaction of $[Zn(dmit)_2]^{2-}$ with the reduced, Ni(II) species such as **1** or **3** gave [CpNi(dmit)] in much lower yield (entries 60 and 61), in accordance with our general rule. The syntheses of the corresponding selenium analogs were performed using the $[Zn(dsit)_2]^{2-}$ complex, and [CpNi(dsit)] was successfully obtained in 5.9% from **1**, 56% from **2** or 35% yield from **3**, respectively (entries 62–64). Finally, the 100% ^{77}Se-enriched [CpNi(dsit)] complex was prepared for EPR studies (see Section 3.4). The product was obtained in 20% overall yield based on the elemental ^{77}Se (Scheme 11) [41]. In addition, the ^{77}Se-enriched [CpNi(bds)] complex has been also synthesized from **2** and $(PPh_4)_2[Zn(bds)_2]$ [41] (Scheme 13).

3. Molecular properties

3.1. Electrochemical properties

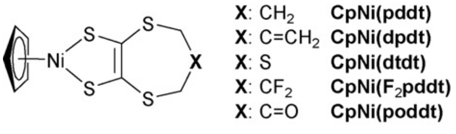
All CpNi(dithiolene) complexes except [CpNi(mnt)] exhibit reversible, one-electron oxidation and reduction waves (Table 7). Of particular note is the large electrochemical window of stability of the radical species, as the $\Delta E = E^{1/2}_{0\rightarrow+1} - E^{1/2}_{-1\rightarrow0}$ values are comprised between 1.0 and 1.43 V. We also observe that the reduction potential of $[CpNi(dithiolene)]^{\bullet}$ complexes, associated with the $-1 \leftrightarrow 0$ redox process, is correlated with the electron-rich or electron-poor nature of the dithiolate ligand, with an electrochemical series which follows that usually observed for the homoleptic square-planar $[Ni(dithiolene)_2]^{2-,1-}$ complexes with the ordering: mnt > tfd > dcmedt > dmit > bdt > dddt > dphedt > dmedt starting with the most electron-poor mnt ligand. For example, within the series of propylenedithio-ethylenedithiolate derivatives (Scheme 14), one observes a similar series for **X** with $CF_2 \geq C{=}O > S > C{=}CH_2 > CH_2$ [35].

On the other hand, the oxidation potential $E^{1/2}_{0\rightarrow+1}$ does not follow these series. This is reflected in the striking evolution of $\Delta E = E^{1/2}_{0\rightarrow+1} - E^{1/2}_{-1\rightarrow0}$. While values as high as 1.40–1.30 V are found on both ends of the series, that is for [CpNi(mnt)] in the one hand, [CpNi(dmedt)] in the other hand, much lower values (≈1.0 V) are observed for [CpNi(dddt)], [CpNi(dmit)] and analogs.

3.2. UV–vis–NIR spectroscopy

All [CpNi(dithiolene)] complexes exhibit a characteristic low-energy absorption band located in the Near Infra-Red (NIR) region between 700 and 1000 nm (Table 7), with an absorption coefficient between 2000 and 6000 $M^{-1} cm^{-1}$. The strong NIR absorptions observed here are particularly surprising for metallo-mono(dithiolene) complexes since complexes such as [(L-*N3*)MoO(dithiolene)] [(L-*N3*) = hydrotris(3,5-dimethyl-1-pyrazolyl)borate] exhibit only very weak absorption in the NIR region with $\varepsilon < 500\ M^{-1} cm^{-1}$ [50]. The other family of mono(dithiolene) complexes investigated so far are the luminescent M(diimine)(dithiolene) ones, such as [Zn(bipy)(bdt)], characterized by a LLCT band in the visible region [10]. [CpM(dithiolene)] complexes of group 9 metal atoms (M = Co, Rh, Ir) normally show visible absorption in the range of 400–700 nm [51] whose electronic absorption are mostly attributed to LMCT. The absorption energy becomes higher in order of the Co < Rh < Ir complexes. The blue shift of the LMCT band can be explained by the increase in the d-orbital energy level of the metal [52].

In order to get some insight on the nature of this NIR absorption band and its correlation with the electrochemical data, the optical gap (ΔE^{opt}) determined from the onset of the low-energy NIR absorption band has been compared with an electrochemical gap (ΔE^{elec}), determined from the onset values of the oxidation potential and reduction potential [26]. Since the detailed spectra are not available for all described complexes, a less precise but still satisfactory correlation can be made here between the $\Delta E = E^{1/2}_{0\rightarrow+1} - E^{1/2}_{-1\rightarrow0}$ value described above in Section 3.1 and the energy (in eV) associated with the maximum of the NIR absorption band (Fig. 1).



Scheme 14.

Table 7
Electrochemical and optical data for [CpNi(dithiolene)] and (diselenolene) complexes, $\Delta E = E^{1/2}_{0\to+1} - E^{1/2}_{-1\to0}$.

Dithiolate	$E^{1/2}_{-1\to0}$ (V)	$E^{1/2}_{0\to+1}$ (V)	ΔE (V)	λ_{max} (nm)	ε ($M^{-1}\ cm^{-1}$)	Ref.
mnt	−0.64	+0.79[a]	1.43	698	2000	[33]
tfd	−0.80	+0.64	1.44	[b]	[b]	[34]
adt	−0.81	+0.52	1.33	[b]	[b]	[34]
dcmedt	−0.86	+0.48	1.34	695	1500	[33]
dmit	−0.72	+0.28	1.00	967	6000	[26,42]
dsit	−0.74	+0.32	1.06	948	3200	[26,42]
dmid	−0.80	+0.26	1.06	[b]	[b]	[42]
oxddt	−1.07	+0.16	1.23	825	1900	[44]
bddt	−1.04	+0.14	1.18	774	2100	[44]
F_2pddt	−0.98	+0.25	1.23	798	2000	[35]
poddt	−0.98	+0.22	1.20	806	1700	[35]
dtdt	−1.02	+0.19	1.21	823	1800	[35]
dpdt	−1.05	+0.12	1.17	840	2400	[35]
pddt	−1.08	+0.07	1.15	848	2100	[35]
dddt	−1.06	−0.02	1.08	1012	4700	[26]
dsdt	−1.06	−0.01	1.07	954	5500	[26]
ddds	−1.07	+0.03	1.10	1000	3600	[26]
bdtodt	−0.83	+0.38	1.21	741	6000	[36]
bdt	−1.00	+0.30	1.30	722	2600	[26]
bds	−1.04	+0.30	1.34	718	2800	[26]
phedt	−1.15	+0.07	1.22	843	3300	[33]
dphedt	−1.16	+0.04	1.20	846	2900	[33]
dmedt	−1.38	−0.04	1.34	835	2600	[33]

[a] Irreversible.
[b] Not reported.

Interesting evolutions can be noted. First, the smallest gaps are found with dithiolate ligands involving outer sulfur atoms (dmit, dddt) in a rigid planar conformation, indicating that they are favoured by a strong delocalisation on the dithiolene ligand. Also, interesting trends are found in the series based on the dddt ligand, when compared with the closely related propylene (pddt) and butylene (bddt) analogs (Scheme 15). Despite closely related chemical structures, the NIR absorptions are found at 1012, 848 and 774 nm for [CpNi(dddt)], [CpNi(pddt)] and [CpNi(bddt)], respectively.

As a first step of a more complete theoretical study on these trends, DFT and TD-DFT calculations were performed on the [CpNi(pddt)] to unravel the exact nature of this NIR optical transition. A standard unrestricted DFT procedure within the Gaussian03 program [53] was initially employed to obtain the fully relaxed ground state. The same computational details, B3LYP hybrid functional [54] and triple-ζ basis set with polarisation functions [55], were used as in our previous calculations on similar [CpNi(dt)] compounds [21,34]. The molecular spinorbital diagram of [CpNi(pddt)] is reported in Fig. 2. The highest occupied α spinorbital is metal ligand antibonding. The main contribution in this SOMO comes from a π* dithiolene, just as the frontier orbitals of the square-planar bis(dithiolene) metal compounds. For the [CpNi(dt)] radicals, the β spinorbital corresponding to the HOMO α is empty and is thus the lowest unoccupied β spinorbital, noted LUMO β. The HOMO β is the matching bonding combination between the CpNi and the dithiolene fragments (Fig. 3).

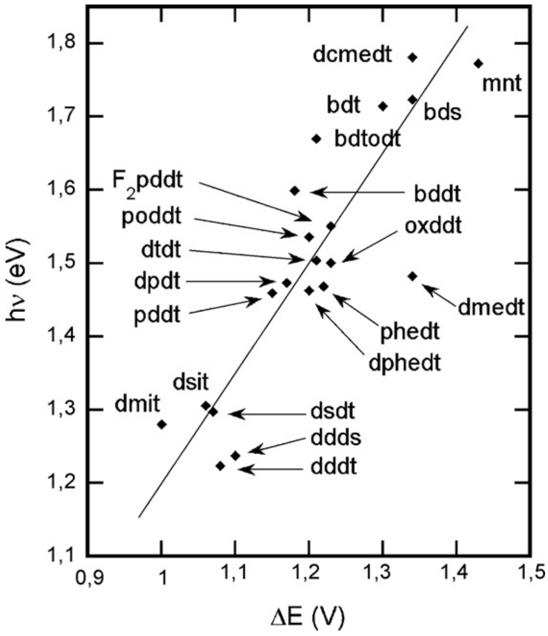
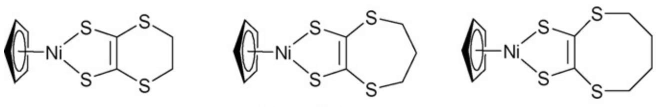


Fig. 1. Correlation between the redox potentials difference $\Delta E = E^{1/2}_{0\to+1} - E^{1/2}_{-1\to0}$ (see Table 7) and the energy ($h\nu$, in eV) associated with the λ_{max} of the NIR absorption band. The line is only a guide to the eye.

Then a time-dependent DFT methodology [53] with the same functional and basis set was used to obtain the fifty first monoelectronic excitations of [CpNi(pddt)]. The only excitation over 600 nm associated with a non-negligible oscillator factor (f = 0.026 compared to 0.0006) shows a maximum at 927 nm, associated to an experimental value of 848 nm, and corresponding to the HOMO β to LUMO β transition at 97%. Therefore, the near Infra-Red absorption band observed recurrently in this family of [CpNi(dt)] radical compounds stem from a M-dt to M-dt* transition of the highest in energy β electron. It is therefore anticipated that it will be highly sensitive to any factor changing the interaction between the two fragments.

3.3. Molecular structures

X-ray crystal structures are available for essentially every [CpNi(dithiolene)] complex, demonstrating their very good



CpNi(dddt) CpNi(pddt) CpNi(bddt)

Scheme 15.

Table 8
Characteristic intra-molecular bond distances and angles in [CpNi(dithiolene)] complexes.

Ligand	Ni–S(Se)	S(Se)–C	C=C	S(Se)–Ni–S(Se)	Cp/NiS_2 dih. ang.	Ref.
Dithiolene						
mnt	2.1255 (8) 2.1282 (8)	1.715 (3) 1.725 (3)	1.354 (4)	94.61 (3)	89.9 (1)	[33]
tfd[a]	2.1179 (9)	1.731 (3)	1.355 (7)	93.25 (6)	96.41 (8)	[34]
adt	2.1167 (17) 2.1225 (15)	1.710 (5) 1.691 (6)	1.320 (7)	93.246 (62)	88.9 (2)	[34]
dmit	2.138 (2) 2.133 (2)	1.706 (8) 1.716 (7)	1.36 (1)	94.97 (8)	86.5	[42]
dmid	2.138 (1) 2.145 (1)	1.718 (3) 1.712 (3)	1.352 (4)	94.90 (3)	88.4 (3)	[42]
oxddt	2.133 (3) 2.121 (3)	1.734 (9) 1.720 (8)	1.353 (13)	91.66 (10)	87.37	[44]
bddt	2.1320 (18) 2.1255 (16)	1.738 (5) 1.739 (6)	1.337 (7)	92.34 (6)	88.87	[44]
F_2pddt	2.1195 (9) 2.1314 (9)	1.724 (3) 1.725 (3)	1.349 (4)	92.58 (3)	89.8	[35]
poddt	2.1244 (9) 2.1258 (9)	1.729 (3) 1.732 (3)	1.357 (4)	93.03 (3)	86.2	[35]
dtdt	2.1209 (7) 2.1337 (8)	1.729 (3) 1.733 (3)	1.356 (4)	92.74 (3)	87.3	[35]
dpdt	2.128 (4) 2.129 (4)	1.807 (11)1.636 (10)	1.387 (6)	92.51 (4)	89.8	[35]
pddt	2.1242 (10) 2.1242 (10)	1.725 (3) 1.726 (3)	1.358 (5)	92.42 (4)	89.3	[35]
dddt[b]	2.125 (2) 2.121 (2)	1.711 (10) 1.744 (9)	1.336 (13)	92.42 (9)	86.9	[26]
dsdt	2.117 (4) 2.132 (4)	1.711 (12)1.740 (11)	1.35 (2)	92.7 (1)	88.4 (6)	[26]
bdtodt	2.1272 (16) 2.1395 (16)	1.739 (6) 1.741 (5)	1.407 (7)	93.74 (6)	89.5 (2)	[36]
bdt[c]	2.1205 (13) 2.1280 (13)	1.731 (5) 1.740 (4)	1.410 (6)	93.93 (5)	84.9	[26]
Diselenolene						
dsit	2.250 (13) 2.250 (18)	1.863 (21)1.871 (10)	1.359 (14)	95.78 (5)	88.2 (3)	[42]
bds[c]	2.239 (2) 2.250 (2)	1.877 (12)1.876 (13)	1.402 (17)1.384 (16)	94.94 (7)93.94 (7)	87.3 (4) 89.7 (4)	[26]
ddds[b]	2.246 (3) 2.236 (2)	1.867 (16)1.887 (15)	1.410 (18)	93.45 (10)	89.5 (4)	[26]

[a] The molecule is located on a mirror plane incorporating the nickel atom and one carbon atom of the Cp ring.
[b] One of the four crystallographically independent molecules.
[c] One of the two crystallographically independent molecules.

propensity to crystallization. In the following, we will not discuss their solid state organization and associated magnetic properties, a topic which has been recently reviewed [20,21]. On the other hand, we provide a comprehensive compilation of available molecular structural features, that is, bond lengths, bond angles and geometrical features which characterize these complexes. In every [CpNi(dithiolene)] complex, the metallacycle is essentially perpendicular to the cyclopentadienyl (Cp) ring (Fig. 4). No distortion of the metallacycle along the S···S hinge are observed, at variance with the Cp_2M(dithiolene) complexes for example [19]. Characteristic bond lengths and angles are reported in Table 8.

At variance with the rigid structure of the $CpNiS_2C_2$ moiety in all [CpNi(dithiolene)] complexes, the substituents on the dithiolene ring can lead to structural flexibility. This is particularly true for the propylenedithio and butylenedithio derivatives such as [CpNi(pddt)] and [CpNi(bddt)], which exhibit strong folding of the outer seven- or eight-member rings (Fig. 4). These distortions are most probably related to the difference of electrochemical and optical gaps identified in the series dddt/pddt/bddt (see Section 3.2).

CpNi(diselenolene) complexes are crystallographically isostructural to the corresponding dithiolene complexes (i.e. dddt *vs.* ddds, dmit *vs.* dsit, bdt *vs.* bds) [26,42]. Differences between the dithiolene and the analogous diselenolene complexes are limited to the expected longer C–Se bonds relative to the C–S bonds. This close proximity is also found in the electronic properties. Electrochemical and optical properties are indeed closely related. In addition, CpNi(dithiolene) are also sometimes isostructural to the CpCo and CpRh complexes with the same dithiolene ligand as observed in [CpNi(bdt)] *vs.* [CpCo(bdt)] [56], [CpNi(mnt)] *vs.* [CpRh(mnt)] [57], [CpNi(oxddt)] *vs.* [CpCo(oxddt)] [58]. On the other hand, even slight modifications of the outer substituents of the dithiolene or diselenolene core do modify strongly the crystal packing, as observed for example with [CpNi(dsdt)] which is not isostructural with [CpNi(dddt)] or [CpNi(ddds)] [26].

3.4. Magnetic properties

The X-band EPR data of the radical [CpNi(dithiolene)] complexes are collected in Table 9. In solution at room temperature, isotropic EPR signals (g = 2.041–2.054) were systematically observed with a line width of ≈10G. A larger spin-orbit coupling in the diselenolene analogs gives rise to broader signals with line widths close to 25G. Note also that the g values of the isoelectronic (17-electron) cobalt complexes $[CpCo(tfd)]^-$ (g = 2.454) [59] and $[CpCo(mnt)]^-$ ($g \approx 2.5$) [60] are much larger, thus demonstrating that the 17-electron Co(dithiolene) complexes have a large spin contribution on the metal centre (formally Co^{II}), while the spin density of the nickel complex is largely delocalised on the ligands.

The frozen solution spectrum of [CpNi(bdt)] (Fig. 5a) shows that the g tensor is axial with $g_{\perp} < g_{//}$. The spectrum obtained with the diselenolene analog [CpNi(bds)] (Fig. 5b) departs from axial sym-

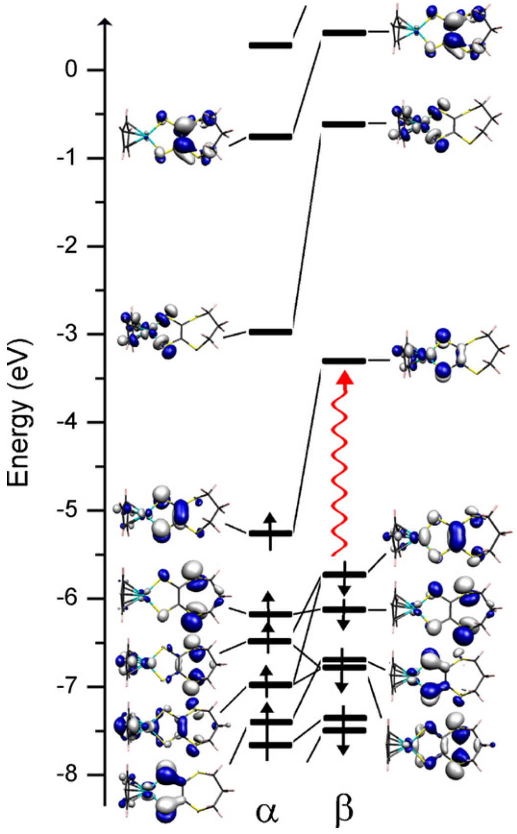


Fig. 2. Molecular spinorbital diagram of [CpNi(pddt)]. Since an unrestricted procedure was employed, the α and β spinorbitals can be slightly different in energy and in their spatial form.

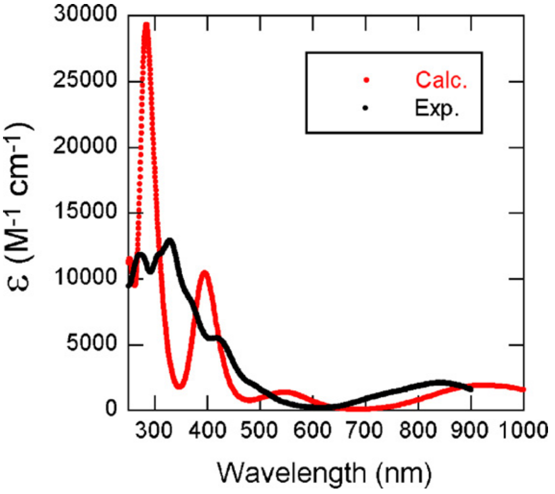


Fig. 3. Theoretical (red) and experimental (black) absorption spectra of [CpNi(pddt)].

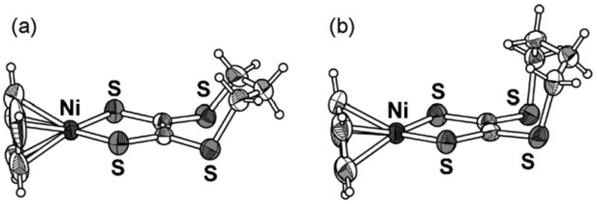


Fig. 4. Ortep views of (a) [CpNi(pddt)] and (b) [CpNi(bddt)], illustrating the strong distortions of the outer seven- and eight-member rings.

Table 9
EPR data collected in solution (g_{iso}) and in frozen solution (g_{max}, g_{int}, g_{min}).

Ligand	g_{iso}	g_{max}	g_{int}	g_{min}	$g_{max} - g_{min}$	Ref.
Dithiolenes						
mnt	2.0487					[33]
tfd	2.0479					[59]
dcmedt	2.0460					[33]
dmit	2.046	2.096	2.028	2.014	0.082	[41]
F_2pddt	2.0529					[35]
poddt	2.0525					[35]
dtdt	2.0524					[35]
dpdt	2.0518					[35]
pddt	2.0514					[35]
dddt	2.042					[26]
dsdt	2.045					[26]
bdt	2.054	2.121	2.024	2.018	0.103	[41]
phedt	2.0412					[33]
dphedt	2.0440					[33]
dmedt	2.0430					[33]
Diselenolenes						
dsit	2.116	2.161	2.137	2.050	0.111	[41]
bds	2.095	2.146	2.110	2.028	0.118	[41]
ddds	2.088					[26]

metry. The resulting principal values of the g tensor are given, when available, in Table 9. For these complexes, the anisotropy ($g_{max} - g_{min}$ in Table 9) is around 0.10; as expected from the room-temperature spectra, the average value for the dithiolene compounds is slightly smaller than for the diselenolene complex. In line with the observations above, we note that the anisotropy ($g_{max} - g_{min}$) is notably smaller for the dmit than for the bdt complex, another illustration of a more extended delocalisation of the spin density on the dmit ligand than in the bdt one.

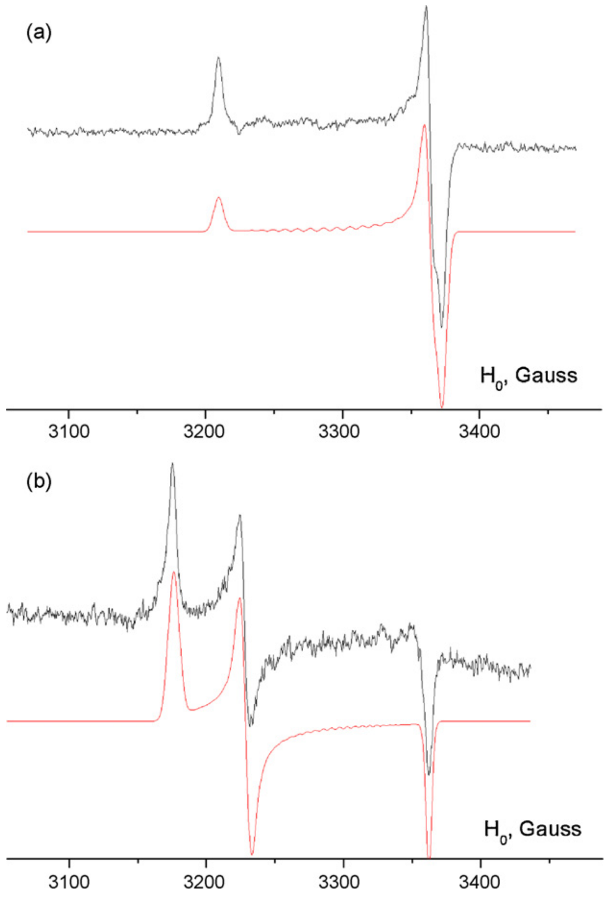


Fig. 5. Experimental (black) and simulated (red) EPR spectra obtained at 77 K with a THF solution of CpNi(bdt) (a) and CpNi(bds) (b) [41].

Table 10
Experimental EPR tensors in [CpNi(diselenolene)] complexes.

Ligand	g tensor				^{77}Se coupling tensor (MHz)			^{77}Se τ_{aniso} (MHz)			^{77}Se A_{iso} (MHz)
	g_1	g_2	g_3	g_{av}	T_1	T_2	T_3	τ_1	τ_2	τ_3	
^{77}bds	2.146	2.110	2.028	2.095	(−)56	(−)33	(+)168	(−)82	(−)59	(+)142	(+)26
^{77}dsit	2.161	2.137	2.050	2.116	(−)59	(−)37	(+)188	(−)90	(−)68	(+)157	(+)31

Hyperfine interactions, when observable on EPR spectra, can provide a direct information about the spin density distribution, allowing for a rationale of the solid state magnetic properties of these radicals [20,21]. However, for [CpNi(dithiolene)] complexes, no proton coupling is resolved on the EPR spectra and, due to the poor abundance of its magnetic isotope (^{33}S, $I = 3/2$, natural abundance = 0.75%), no sulfur coupling could be detected (see Fig. 5a for example). Therefore, substitution of sulfur atoms by selenium atoms appeared to be the most pertinent method: ^{77}Se has a natural abundance of 7.3% and its spin number is only 1/2. Unfortunately, the large line width of the EPR signals of [CpNi(bds)] (Fig. 5b) precluded the detection of the corresponding satellite lines. In order to circumvent this lack of information, 100% ^{77}Se-enriched samples of [CpNi(bds)] and [CpNi(dsit)], noted [CpNi(^{77}bds)] and [CpNi(^{77}dsit)] in the following, have been prepared by an original method (see Scheme 13 in Section 2.7), allowing for a successful observation of ^{77}Se couplings from their frozen solution spectra (Fig. 6) [41]. The resulting experimental ^{77}Se isotropic and anisotropic coupling constants are reported in Table 10.

DFT calculations have been performed on these two diselenolene complexes in order to rationalize the experimental EPR observations, as several recent reports have shown that their are now able to predict not only the hyperfine couplings but also the g tensors with a good accuracy [61]. The g_{min} eigenvector was found to be oriented perpendicular to the Ni-containing ring, and the two other principal directions oriented parallel and perpendicular to the chalcogen–chalcogen direction of this ring. The spin delocalisation on the two selenium atoms was roughly estimated by comparing the experimental ^{77}Se couplings with the atomic constants [62]. This led, for [CpNi(^{77}bds)], to a very small spin density in the s-orbitals of Se (ρ_s) (26/20120 = 0.1%) and to an appreciable p-character (ρ_p) (142/982 = 14%). Similar values are found for [CpNi(^{77}dsit)]: $\rho_s = 0.1\%$, $\rho_p = 16\%$ [41]. These experimentally determined spin densities on the selenium atoms of the diselenolene complexes were found in very good agreement with those determined from DFT calculations.

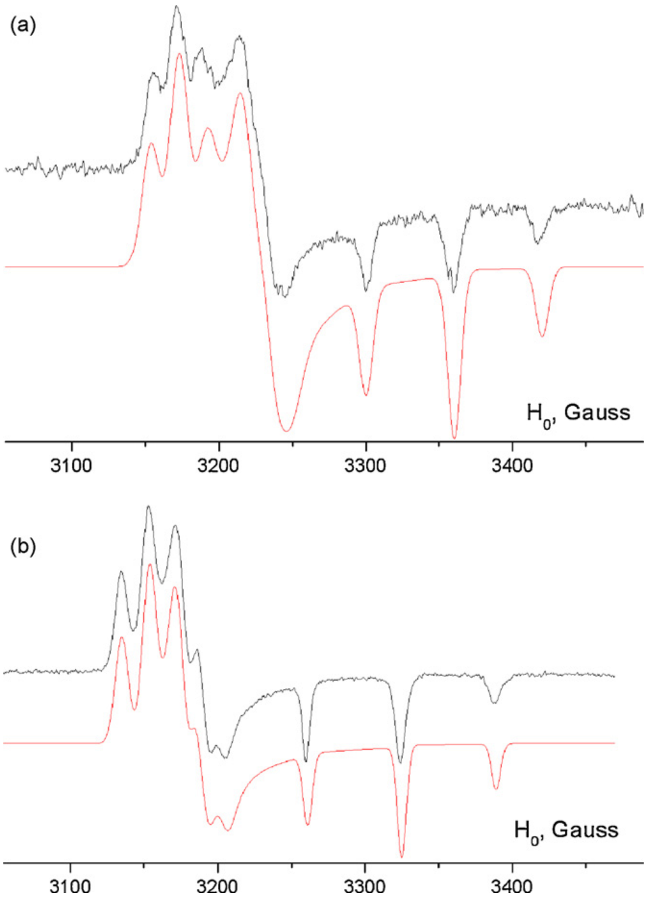


Fig. 6. Experimental (black) and simulated (red) EPR spectra obtained at 77 K with a THF solution of ^{77}Se-enriched [CpNi(^{77}bds)] (a) and [CpNi(^{77}dsit)] (b) [41].

Table 11
Calculated spin density distribution in [CpNi(dithiolene)] and (diselenolene) complexes.

Ligand	2S or 2Se	Ni	Cp	Others	Ref.
Dithiolenes					
mnt	0.34	0.43	0.21	0.02	[34]
tfd	0.34	0.41	0.23	0.03	[34]
adt	0.36	0.38	0.21	0.05	[34]
bdt	0.30	0.49	0.20	0.01	[41]
bdt	0.32	0.42	0.21	0.05	[26]
dmit	0.46	0.29	0.15	0.10	[41]
dddt	0.40	0.28	0.12	0.20	[26]
Diselenolenes					
bds	0.20	0.60	0.20	0.01	[41]
dsit	0.34	0.45	0.17	0.04	[41]

Actually, spin density calculations were also reported for several dithiolene complexes. They have been collected all together in Table 11 where several interesting trends appear from their comparison. While the spin density on the nickel atom amounts to ≈40% in most complexes (up to 45 and 60% in the diselenolene ones), it is less than 30% in the dmit and dddt complexes with a transfer to the chalcogen atoms of the dithiolene ligand, also involving the outer substituents of the NiS_2C_2 metallacycle. This enhanced delocalisation is most probably at the origin of the specific behaviour of these two [CpNi(dmit)] and [CpNi(dddt)] complexes, as already noted from the electrochemical/optical correlations (Fig. 1).

On the other hand, we also note that all complexes exhibit a sizeable spin density on the cyclopentadienyl ring, an original feature in organometallic metallocene chemistry. This large delocalisation on the Cp ring has been shown to be at the origin of strong antiferromagnetic coupling interactions in the solid state, when two radical complexes crystallize in a Cp···Cp face-to-face motif [26,34], as indeed experimentally observed in [CpNi(adt)], [CpNi(bdt)] and [CpNi(bds)].

4. Conclusions and perspectives

Different synthetic routes toward the formally Ni$^{(\text{III})}$ radical complexes [CpNi(dithiolene)] (and their diselenolene analogs) have been compared, based on the reaction of CpNi precursors with various dithiolene salts. The highest yields are obtained with an appropriate redox match, that is a CpNi$^{(\text{II})}$ precursor such as nickelocene with a formally Ni$^{(\text{IV})}$ [Ni(dithiolene)$_2$]^0 neutral complex, or the $Ni^{(III)}$ nickelocenium salt with a formally $Ni^{(III)}$ $[Ni(dithiolene)_2]^-$ monoanionic complex. These methods provide now a readily access, in good yields, to these soluble radical species. These complexes crystallize nicely and were all structurally characterized; they systematically exhibit a recurrent geometry with a planar NiS_2C_2 metallacycle, perpendicular to the cyclopentadienyl ring. The electrochemical and optical properties (UV–vis–NIR spectroscopy) of more than twenty different complexes were compared. They exhibit a small optical gap with a low-energy absorption band in the Near Infra-Red region, between 700 and 1000 nm. The smaller electrochemical and optical gap found in the [CpNi(dmit)] and [CpNi(dddt)] complexes is correlated with an extensive delocalisation of the spin density in these complexes, while the other members of the series are characterized with a larger and sizeable spin density on the cyclopentadienyl ring. Preliminary TD-DFT calculations performed on the [CpNi(pddt)] complex shows that the NIR absorption band finds its origin in a HOMO $\beta \rightarrow$ LUMO β transition, where the HOMO β and LUMO β are respectively the bonding and antibonding combinations of the CpNi and dithiolene fragments.

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