Various preparations of the neutral radical \([\text{CpNi(dddt)}]\) complex (dddt = 5,6-dihydro-1,4-dithiin-2,3-dithiolate) were investigated with CpNi sources, \([\text{Cp2Ni}], [\text{Cp2Ni}](\text{BF}_4), [\text{CpNi(CO)}]_2, \text{and [CpNi(cod)}](\text{BF}_4), \) and dithiolene transfer sources, OC(dddt), the naked dithiolate (dddt2-), the monoanion of square-planar Ni dithiolene complex (NBu4)[Ni(dddt)2], and the neutral complex [Ni(dddt)2]. The reaction of [CpNi(cod)](BF4) with (NBu4)[Ni(dddt)2] gave the highest yield for the preparation of [CpNi(dddt)] (86%). [CpNi(ddds)] (ddds = 5,6-dihydro-1,4-dithiin-2,3-diselenolate), [CpNi(dsdt)] (dsdt = 5,6-dihydro-1,4-diselenin-2,3-dithiolate), [CpNi(bdt)] (bdt = 1,2-benzenedithiolate), and [CpNi(bds)] (bds = 1,2-benzenediselenolate) were synthesized by the reactions of [Cp2Ni] with the corresponding neutral Ni dithiolene complexes [Ni(ddds)2], [Ni(dsdt)2], [Ni(bdt)2], and [Ni(bds)2], respectively. The five, formally NilII, radical complexes oxidize and reduce reversibly. They exhibit, in the neutral state, a strong absorption in the NIR region, from 1000 nm in the dddt/ddds/dsdt series to 720 nm in the bdt/bds series with \(\varepsilon\) values [...]
[CpNi(dithiolene)] (and Diselenolene) Neutral Radical Complexes

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Various preparations of the neutral radical [CpNi(dddt)] complex (dddt = 5,6-dihydro-1,4-dithiin-2,3-dithiolate) were investigated with CpNi sources, [Cp2Ni], [Cp2Ni][BF4], [CpNi(CO)]2, and [CpNi(cod)][BF4], and dithiolene transfer sources, O=C(dddt), the naked dithiolate (dddt−), the monoanion of square-planar Ni dithiolene complex (NBu4)[Ni(dddt)]−, and the neutral complex [Ni(dddt)]0. The reaction of [CpNi(cod)][BF4] with (NBu4)[Ni(dddt)]− gave the highest yield for the preparation of [CpNi(dddt)] (86%). [CpNi(ddds)] (ddds = 5,6-dihydro-1,4-dithiin-2,3-diselenolate), [CpNi(dsdt)] (dsdt = 5,6-dihydro-1,4-diselenin-2,3-dithiolate), [CpNi(bdt)] (bdt = 1,2-benzenedithiolate), and [CpNi(bds)] (bds = 1,2-benzenediselenolate) were synthesized by the reactions of [Cp2Ni] with the corresponding neutral Ni dithiolene complexes [Ni(ddds)]2, [Ni(dsdt)]2, [Ni(bdt)]2, and [Ni(bds)]2, respectively. The five, formally NiIII, radical complexes oxidize and reduce reversibly. They exhibit, in the neutral state, a strong absorption in the NIR region, from 1000 nm in the dddt/ddds/dsdt series to 720 nm in the bdt/bds series with ε values between 2500 and 5000 M−1 cm−1. The molecular and solid state structures of the five complexes were determined by X-ray structure analyses. [CpNi(dddt)] and [CpNi(ddds)] are isostructural, while [CpNi(dsdt)] exhibits a closely related structure. Similarly, [CpNi(bdt)] and [CpNi(bds)] are also isostructural. Correlations between structural data and magnetic measurements show the presence of alternated spin chains in [CpNi(dddt)], [CpNi(ddds)], and [CpNi(dsdt)], while a remarkably strong antiferromagnetic interaction in [CpNi(bdt)] and [CpNi(bds)] is attributed to a Cp···Cp face-to-face σ overlap, an original feature in organometallic radical complexes.

Introduction

Dithiolene complexes with a central Ni atom are the most investigated of the metal dithiolene complexes. Since the first square-planar Ni bis(dithiolene) complex reported in 1960,1 Ni dithiolene complexes have been thoroughly investigated from the viewpoint of optical,2 magnetic,3 and conductive studies.4 Most of these Ni dithiolene complexes are of the square-planar type,5 and they are well-known to exist in several well-defined oxidation states.6 Heteroleptic complexes associating dithiolate and cyclopentadienyl ligands have been much less investigated. Such Cp−metal−dithiolene complexes can be classified into four main categories:7 the 2:2 Cp/dithiolene complexes formulated as [CpM(dithiolene)]2 (M = group 5, 6, and 8 metals), the 2:1 Cp/dithiolene complexes [Cp2M(dithiolene)] (M = group 4−6 metals), the...
1:2 Cp/dithiolene complexes [CpM(dithiolene)₂] (M = group 4−7 metals), and the 1:1 Cp/dithiolene complexes [CpM- (dithiolene)] (M = group 9 and 10 metals). The CpNi dithiolene complexes are included into the fourth category but are quite rare. King first reported the synthesis of [CpNi–(tfd)] (tfd = 1,2-bis(trifluoromethyl)dithiolate, Cp = η⁵ cyclopentadienyl), and Wharton reported the η⁴-cyclobutadiene Ni dithiolene complex which is formulated as [(η⁴-C₅R₅)Ni(mnt)] (mnt = maleonitriledithiolate). More recently, Faulmann et al. synthesized [CpNi(dmit)] (dmit = 1,3-dithiol-2-thione-4,5-dithiolate) serendipitously from the reaction of [CpNi(BF₄)] with Na[Ni(dmit)]. The expected salt [CpNi][Ni(dmit)] was not obtained but rather the neutral paramagnetic complex [CpNi(dmit)]. We have recently started a thorough investigation of the chemistry of the CpNi dithiolene complexes, for the following attractive reasons: (1) their synthetic methods are unique (Schemes 1−3) and provide new organometallic reactions; (2) these complexes are paramagnetic in the neutral state (formally NiⅢ), hence strong magnetic interactions in the crystalline solid state can be anticipated from the absence of any counterion; (3) these complex are quite soluble in organic solvents thanks to the Cp ligand, and single crystals are easily obtained by recrystallization without need for electocrystallization experiments; and (4) some of these complexes exhibit an electronic absorption in the near-IR region, an original feature also observed in the square-planar Ni dithiolene complexes. Therefore, the CpNi(dithiolene) complexes are very attractive from the organometallic, magnetic, and optical points of view. We report here a comparative investigation of different synthetic methods for the preparation of such complexes based on the novel complex [CpNi(dddt)] (dddt = 5,6-dihydro-1,4-dithiin-2,3-dithiolate) and describe the preparation of the selenium-containing analogues CpNi(ddds) and CpNi(ddt), together with similar complexes based on benzenedithiol (i.e., CpNi(bdt) and CpNi(bds)). The X-ray crystal structures and electrochemical and magnetic properties of the five novel CpNi dithiolene complexes have been investigated in detail with special emphasis on (i) a NIR absorption band observed in all complexes but at different energies and (ii) the antiferromagnetic interactions present in the crystalline phases, as reflected by the analysis of the temperature dependence of the magnetic susceptibility.

Results and Discussion

Syntheses of CpNi Dithiolene and Diselenolene Complexes. The described syntheses of these formally NiⅢ CpNi dithiolene complexes involve a CpNi source and a dithiolene transfer source, together with an appropriate redox match between both partners. The formers can be the η⁴ cyclopentadienylnickel carbonyl dimer [CpNi(CO)]₂, the NiⅢ nickelocene [Cp₂Ni], or the NiⅢ nickelocenium (Cp₂Ni)(BF₄). Dithiolene sources can be 1,2-dithi ete (or 1,2-dithiole), or the square-planar metal dithiolene complexes, [M(dithiolene)]²⁺ (M = Ni, Pd, and Pt; n = 0, −1) and [Pt(dithiolene)(dppe)] (dppe = bis(diphenylphosphino)ethane). Some examples of those reactions are shown in Schemes 1−3. In Scheme 1, the 2e oxidized forms of the dithiolate react with low-valent CpNi sources (NiⅠ in [CpNi(CO)]₂, NiⅢ in [CpNi], while Scheme 2 involves the reaction of a NiⅢ CpNi source with a protected dithiolate. Satisfactory yields were only reported in those reactions involving square-planar nickel dithiolene complexes in their anionic or neutral forms, as described in Scheme 3.

For the synthesis of the new complex [CpNi(dddt)] (dddt = 5,6-dihydro-1,4-dithiin-2,3-dithiolate) described here, we have therefore investigated different combinations of CpNi and dithiolene transfer sources. The results of these reactions are collected in Table 1 and will be discussed shortly, while details of each entry can be found in the Experimental Section. Entries 1−4 involve the thermal or photochemical activation of a 1,3-dithiole-2-one to generate, as a reactive
intermediate, the corresponding 1,2-dithiolene or 1,2-dithiete (shown in Scheme 1),
but the isolated yields do not exceed 30% regardless of the nature of the CpNi source
(CpNi or [CpNi(CO)]2). The shorter reaction time obtained with [CpNi(CO)]2 (entry 3) can be attributed to the concomitant thermal activation of [CpNi(CO)]2 for decarbonylation. Entries 5–7 involve the reaction of the “naked” dithiolene dddt2− with either the NiII [CpNi] or [CpNi(cod)]-BF4 or the NiIII [CpNi]BF4 complexes, but the yields are not satisfactory (<28%). Finally, the best yields (60–85%) were obtained as described before11,12 with the square planar monoanionic or neutral nickel dithiolene complexes, as described in entries 8–13. Note, however, that the proper CpNi source has to be found in each case since, for example, the NiII [CpNi] neutral complex does not react with [Ni(dddt)] (entry 9), while an 86% yield of [CpNi(dddt)] is obtained when using the NiII [CpNi(cod)]BF4 salt (entry 10), introducing the CpNi(cod)+ cationic species as a novel, efficient source of CpNi in these syntheses.20 Similarly, the neutral, formally NiIV, [Ni(dddt)]2 complex21 was found to be inert to the NiII [CpNi]BF4 (entry 12), while it reacts efficiently with the reduced [CpNi] or [CpNi(CO)]2 neutral complexes (entries 11 and 13).

This last method was therefore used for the syntheses of the new complexes described here, [CpNi(bdt)] (51% yield, entry 16) and its diselenolene analogue [CpNi(bds)] (40% yield, entry 17). In the reaction of [CpNi] with [Ni(bdt)], the oligomer of the Ni monodithiolene [Ni(bdt)]n (n = 6) was isolated by column chromatography in a 31% yield.22 Generally, the neutral square-planar dithiolene complex has stable “dithiolate” and reactive “dithioke tone” ligands, which are exhibited as [MII(dithiolate)(dithioketone)] (M = Ni, Pd and Pt).23 We assume that the coordinated dithioke tone moiety reacted with a CpNi source to form the CpNi dithiolene complex, and then the remaining Ni(dithiolate) moiety is oligomerized. Some dithioke tone transfer reactions using the square-planar complex [Ni(S2C2Ph2)]2 have been

(22) This oligomer was detected by TOF-Mass (no matrix): 1192 ([Ni-bdt]3−).
Table 1. Syntheses of CpNi Dithiolene Complexes

<table>
<thead>
<tr>
<th>Entry</th>
<th>Dithiolene Source</th>
<th>CpNi Source</th>
<th>Molar Ratio</th>
<th>Solvent</th>
<th>Condition</th>
<th>Time (h)</th>
<th>Product</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>O=C(dddtt)</td>
<td>[Cp,Ni]</td>
<td>1:1</td>
<td>Toluene</td>
<td>Reflux</td>
<td>24</td>
<td>[CpNi(ddtt)]</td>
<td>29</td>
</tr>
<tr>
<td>2</td>
<td>O=C(ddtt)</td>
<td>[Cp,Ni]</td>
<td>1:1</td>
<td>Toluene</td>
<td>hv</td>
<td>24</td>
<td>[CpNi(ddtt)]</td>
<td>30</td>
</tr>
<tr>
<td>3</td>
<td>O=N(ddtt)</td>
<td>[CpNi(CO)]</td>
<td>1:1</td>
<td>Methanol</td>
<td>Room Temp</td>
<td>0.5</td>
<td>[CpNi(ddtt)]</td>
<td>28</td>
</tr>
<tr>
<td>4</td>
<td>O=C(ddtt)</td>
<td>[CpNi(CO)]</td>
<td>1:1</td>
<td>Methanol</td>
<td>Room Temp</td>
<td>0.5</td>
<td>[CpNi(ddtt)]</td>
<td>28</td>
</tr>
<tr>
<td>5</td>
<td>Na₂(ddtt)</td>
<td>[Cp,Ni]</td>
<td>1:1</td>
<td>Methanol</td>
<td>Room Temp</td>
<td>0.5</td>
<td>[CpNi(ddtt)]</td>
<td>28</td>
</tr>
<tr>
<td>6</td>
<td>Na₂(ddtt)</td>
<td>[CpNi(BF₄)]</td>
<td>1:1</td>
<td>Methanol</td>
<td>Room Temp</td>
<td>0.5</td>
<td>[CpNi(ddtt)]</td>
<td>17</td>
</tr>
<tr>
<td>7</td>
<td>Na₂(ddtt)</td>
<td>[CpNi(Ni)(CO)]</td>
<td>1:1</td>
<td>Methanol</td>
<td>Room Temp</td>
<td>0.5</td>
<td>[CpNi(ddtt)]</td>
<td>17</td>
</tr>
</tbody>
</table>

*No reaction. Isolated yield.

Table 2. Redox Potentials of CpNi Dithiolene and Diselenolene Complexes (E vs Fe³⁺/Fe²⁺)

<table>
<thead>
<tr>
<th>Reaction</th>
<th>E₁/₂ (red) (V)</th>
<th>ΔEₚ (mV)</th>
<th>ΔEₚ (mV)</th>
<th>E₁/₂ (ox) (V)</th>
<th>ΔEₚ (mV)</th>
<th>ΔEₚ (mV)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>[CpNi(S₂C₂Me₂)]</td>
<td>−1.38</td>
<td>b</td>
<td>b</td>
<td>−0.04</td>
<td>b</td>
<td>b</td>
<td>12</td>
</tr>
<tr>
<td>[CpNi(S₂C₂Ph₂)]</td>
<td>−1.07</td>
<td>72</td>
<td>108</td>
<td>+0.03</td>
<td>74</td>
<td>104</td>
<td>this work</td>
</tr>
<tr>
<td>[CpNi(ddtt)]</td>
<td>−1.06</td>
<td>72</td>
<td>106</td>
<td>−0.02</td>
<td>74</td>
<td>106</td>
<td>this work</td>
</tr>
<tr>
<td>[CpNi(ddtt)]</td>
<td>−1.06</td>
<td>66</td>
<td>86</td>
<td>−0.01</td>
<td>68</td>
<td>82</td>
<td>this work</td>
</tr>
<tr>
<td>[CpNi(ddtt)]</td>
<td>−1.04</td>
<td>74</td>
<td>108</td>
<td>+0.30</td>
<td>74</td>
<td>104</td>
<td>this work</td>
</tr>
<tr>
<td>[CpNi(ddtt)]</td>
<td>−1.00</td>
<td>68</td>
<td>92</td>
<td>+0.30</td>
<td>72</td>
<td>88</td>
<td>this work</td>
</tr>
<tr>
<td>[CpNi(ddtt)]</td>
<td>−0.72</td>
<td>200</td>
<td>200</td>
<td>+0.28</td>
<td>200</td>
<td>200</td>
<td>this work</td>
</tr>
<tr>
<td>[CpNi(ddtt)]</td>
<td>−0.74</td>
<td>200</td>
<td>200</td>
<td>+0.32</td>
<td>200</td>
<td>200</td>
<td>this work</td>
</tr>
<tr>
<td>[CpNi(ddtt)]</td>
<td>−0.64</td>
<td>200</td>
<td>200</td>
<td>+0.79</td>
<td>200</td>
<td>200</td>
<td>this work</td>
</tr>
</tbody>
</table>

*E₁/₂ = (Eₚ + Eₚ)/2, ΔE = |Eₚ − Eₚ|, ΔEₚ = |Eₚ − Eₚ|. Isolated yield. 1Irreversible.

coupling with the heavier selenium atoms. Preliminary DFT calculations [UB3LYP/6-31G(d,p)] were performed to estimate the g variation caused by the replacement of a dithiolene moiety by a diselenolene moiety: passing from [CpNi(bdt)] to [CpNi(bds)] causes an increase in the calculated g₂₀ value equal to 0.028, which is slightly smaller than the experimental value of 0.041. It is worth mentioning that the g values of CpNi dithiolene and diselenolene complexes are smaller than those reported for the one-electron-reduced species of the CpCo dithiolene complexes, the spin is strongly localized on the central metal, while in the CpNi dithiolene complexes, it appreciably delocalizes on the dithiolene ligand. Work is in progress to prepare those selenolene complexes marked with the ⁷⁷Se isotope.

**Electronic Transitions.** Electronic absorption spectra were measured in a CH₂Cl₂ solution between 300 and 1500 nm


for the five new complexes, as well as for [CpNi(dm3it)] and [CpNi(dsit)]. As shown in Figure 1, in addition to the UV–vis absorption peaks, all complexes exhibit a strong NIR (near-infrared) absorption (Table 3), observed around 1000 nm in the dddt/ddds/ddsd series, 955 nm in the dm3it/dsdt series, and 720 nm in the bdt/bds series, while a much lower absorption wavelength had been reported for [CpNi(mnt)] at 700 nm.22 Such strong NIR absorptions have been known for a long time34 in neutral or anionic square-planar bis-(dithiolene) complexes and were investigated for their applications as Q-switching laser dyes.35 Molar extinction coefficients as high as 8 000 M–1 cm–1 were even reported in neutral [M(R,R′timdt)2] (R,R′timdt = N,N′-disubstituted imidazolidine-2,4,5-trithione).36 Accordingly, the square-planar bis(dithiolene) complexes have been the subject of intense theoretical investigations in relation to their electronic structures and can be described as an essentially ligand one-electron promotion that possesses a small degree of LMCT character.37,38

The strong NIR absorptions observed here are particularly surprising for metallo-mono(dithiolene) complexes since complexes such as (L−N2)MoO(dithiolene) [(L−N2) = hydrotris(3,5-dimethyl-1-pyrazolyl)borate] exhibit only very weak absorption in the NIR region with ε < 500 M–1 cm–1.39 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.40 To get some, at least, qualitative insight on the electronic structures of these complexes, the nature of the NIR absorption band and its evolution with the dithiolene ligand and the optical and electrochemical data were analyzed in more detail to evaluate the HOMO/LUMO gap and associated energies in the different complexes. From the onset values of the oxidation potential and reduction potential, an electrochemical gap (Eox−Ered) can be determined and compared with the optical gap (Eop) determined from the onset of the low-energy NIR absorption band. We note (Table 4) that the electrochemically determined gaps are approximately the same as the optically determined ones with larger values systematically observed for the bdt/bds series, as well as for the mnt complex. The HOMO values were experimentally estimated by the onset of the oxidation potential, taking the known reference level for ferrocene, 4.8 eV below the vacuum level,41 according to the following equation: HOMO = −(Eox onset − Fc+/Fc) = −(Eox (ferrocene)) − 4.8 with Eox onset in V vs Fc+/Fc, Eox (ferrocene) = 0 V vs Fc+/Fc.

allowed us to infer that even smaller ones with their associated low energy NIR absorption band could be found with very electron-rich dithiolates such as those used by Mueller-Westerhoff in square-planar nickel dithiolene complexes. For instance, on the basis of the evolution of the $E_{1/2}$ (red) for the [CpNi(dithiolene)] series, the S/Se substitution in the metallacycle does not substantially modify the packing of the molecules. This contrasts with the square planar bis(dithiolene) complexes such as Ni(dmit)$_2$, Ni(dddt)$_2$, or Ni(bdt)$_2$, $n = -2, -1, 0$, where the S/Se substitution to the corresponding Ni-(dmit)$_2$, Ni(ddds)$_2$, or Ni(bds)$_2$ does not generally provide isostructural salts. Most probably here, the Cp ring partially hides the chalcogen atoms engaged in the nickel coordination. 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 here for [CpNi-(dsdt)] which is not isostructural with [CpNi(dddt)] or [CpNi(bdt)].

Intramolecular bond lengths are collected in Table S1 in the Supporting Information, together with those of monoanionic square planar bis-(dithiolene) or bis-(selenolene) complexes for comparison purposes. The Ni–S bond lengths in [CpNi(dddt)], [CpNi(dsdt)], and [CpNi(bdt)] ($\sim 2.12$ Å) are shorter than the Ni–Se bond lengths in [CpNi(dsds)] and [CpNi(bds)] ($\sim 2.25$ Å). Similar tendencies have been observed in [CpNi(dmit)] versus [CpNi(dsit)],[10,11] [Ni(dddt)$_2$] versus [Ni(dsdt)$_2$],[26,41] and [Ni(bdt)$_2$] versus [Ni(bds)$_2$].[26,41] The difference between the Ni–S and Ni–Se bond lengths ($\sim 0.13$ Å) is almost equal to that between the atomic covalent radius of sulfur and selenium. The bond lengths of the C=C double bond in the dithiolene ligands are intermediary between a C–C single and C=C double bond length, illustrating that the oxidation of the formally Ni(II) CpNi(dithiolene) complex to the neutral radical [CpNi(dithiolene)] essentially affects the dithiolene ligand. Furthermore, the C1–C2 lengths in [CpNi(bdt)] and [CpNi(bds)] ($\sim 1.4$ Å) is slightly longer than those of the other CpNi dithiolene complexes (1.33–1.38 Å). This result is explained by not only π conjugation in a dithiolene ring but also the π conjugation of benzene ring, and this fact is also found in [Ni(bdt)$_2$] and [Ni(bds)$_2$] (C1–C2 = 1.39 Å).[42] The largest

![ORTEP drawing of [CpNi(dsdt)]. Thermal ellipsoids are drawn at the 50% probability level.](Image 74x452 to 274x600)

![ORTEP drawing of the two crystallographically independent molecules in the diselenolene complex [CpNi(bds)]. Thermal ellipsoids are drawn at the 50% probability level.](Image 74x632 to 274x744)
deviations from the nickel–dithiolene and –disselenolene planes are very small (See Table S2 in Supporting Information), namely, these five-membered metallacycles are fully planar. This fact can be seen for the pseudoaromaticity of nickel–dithiolene and –disselenolene rings.\textsuperscript{42} In addition, the Ni–bdt (nickel–dithiolene with benzene) and the Ni–bds moieties are almost planar (largest deviations = 0.0376 Å in [CpNi(bdt)] and 0.0587 Å in [CpNi(bds)]). The dihedral angles between Cp and nickel–dithiolene (or –disselenolene) are almost a right angle. This result indicates that they are typical two-legged piano-stool geometries.

Although [CpNi(bdt)] and [CpNi(bds)] are monomers, some dimer structures have been reported in [CpCo(bdt)]\textsubscript{2},\textsuperscript{43} [CpCo(bds)]\textsubscript{2},\textsuperscript{44} [Cp*Rh(bdt)]\textsubscript{2} (Cp* = \(\eta^2\)-pentamethyl cyclopentadienyl),\textsuperscript{45} [(\(\eta^6\)-C\textsubscript{6}R\textsubscript{6})Ru(bdt)]\textsubscript{2},\textsuperscript{46} and [Cp*Ru(bdt)]\textsubscript{2}.\textsuperscript{47} In these Co, Rh, and Ru complexes, the corresponding monomers have electron-poor metal centers (formal 15- or 16-electrons). As already determined above from the electrochemical behavior, we assume that the CpNi dithiolene and diselenolene complexes are not dimerized because these complexes have more electron-rich metal centers (formal 17-electrons) than those of the Co, Rh, and Ru dithiolene complexes.

Solid State Structures and Magnetic Behavior. In the solid state, the isostructural [CpNi(dddt)] and [CpNi(ddds)] radical complexes organize into columns running along the c axis (Figure 4), with intermolecular interactions between columns which only involve the outer sulfur atoms of the dithiine rings. The shortest S...S intermolecular contacts are observed at 3.81 and 3.86 Å, and it is anticipated that the magnetic interactions through these S...S contacts are most probably weak since the SOMO in such complexes, as already reported in [CpNi(dmit)],\textsuperscript{11} is essentially localized on the NiS\textsubscript{2}C\textsubscript{2} or NiSe\textsubscript{2}C\textsubscript{2} metallacycles.

On the other hand, within the columns running along c (Figure 5), short intermolecular S...S, Se...S, and Se...Se contacts involving chalcogen atoms of the metallacycles are now identified, giving rise in both complexes to spin chains running along c, with S...S contacts of 3.75 and 4.05 Å in [CpNi(dddt)] and Se...Se contacts of 3.84 and 3.96 Å in [CpNi(ddds)]. The situation is notably different in [CpNi(dsdt)] where similar but uniform spin chains are found to run along the a axis (Figure 6).

The temperature dependence of the magnetic susceptibility (Figure 7) of [CpNi(dddt)], [CpNi(ddds)], and [CpNi(dsdt)] reflects these different structural organizations. It exhibits indeed a Curie–Weiss type behavior in the high-temperature regime with \(\theta_{dddt} = -46\) K, \(\theta_{ddds} = -36\) K, and \(\theta_{dsdt} = -58\) K, demonstrating the presence of strong antiferromagnetic interactions between the radical moieties, with stronger interactions in the dsdt complex. A susceptibility maximum is observed in all complexes, at 27 K in [CpNi(dddt)], 25 K in [CpNi(ddds)], and at a higher temperature (45 K), as anticipated from the \(\theta_{dsdt}\) value, in [CpNi(dsdt)]. No field dependence of the susceptibility below these temperature maxima was observed, ruling out the possibility of an ordered antiferromagnetic ground state in the three compounds.

On the basis of the structure descriptions given above for the two isostructural [CpNi(dddt)] and [CpNi(ddds)] complexes, an alternated chain model with \(J_{dddt}/k = -65\) K (45 cm\textsuperscript{-1}), \(J_{ddds}/k = -66\) K (46 cm\textsuperscript{-1}), \(\alpha_{dddt} = \alpha_{ddds} = 0.7\). On the other hand, a Heisenberg uniform chain model
can be considered to fit the magnetic data of [CpNi(dsdt)]. However, such a model could not fit satisfactorily the experimental data, and a slight alternation had to be introduced in the chain model \((\alpha = 0.9)\) to take into account the activated part of the susceptibility below \(T_{\text{max}}\), yielding a \(JK\) value of \(-77\) K \((53\ \text{cm}^{-1})\). This failure to fit the magnetic susceptibility down to low temperatures with the Bonner–Fisher model probably reflects a tendency of the uniform chains identified in the room-temperature X-ray crystal structure of [CpNi(dsdt)] to undergo a weak dimerization upon cooling which opens a gap in the energy dispersion of the chain. Indeed, upon dimerization, an alternated spin chain is formed, whose magnetic behavior is characterized by a singlet ground state and an activated susceptibility in the low-temperature region.

As mentioned above, [CpNi(bdt)] and [CpNi(bds)] are isostructural and crystallize with two crystallographically independent molecules, A and B in the following. In the solid state, the radical molecules organize perpendicular to each other (Figure 8), and short intermolecular chalcogen•••chalcogen contacts can hardly be identified as the shortest intermolecular S•••S distances are 4.42 Å between the A molecules and 4.75 Å between the B molecules in [CpNi(bdt)], and the shortest Se•••Se intermolecular distances are found at 4.25 Å between the A molecules and 4.65 Å between the B molecules in [CpNi(bds)].

It is therefore anticipated that the radical species are essentially independent from each other and that the temperature dependence of their magnetic susceptibility should follow a Curie or Curie−Weiss law. As shown in Figure 9, this is absolutely not the case: a broad susceptibility maximum around room temperature is observed together with a Curie contribution at the lowest temperatures. This behavior testifies for the presence of strong antiferromagnetic interactions, which cannot be attributed here to chalcogen•••chalcogen or chalcogen•••nickel interactions. A closer inspection of the crystal structures of [CpNi(bdt)] and [CpNi(bds)] reveals an original feature which has not been seen before in these series; an almost face-to-face arrangement of the Cp rings of molecules A and B (Figure 10) with C•••C intermolecular distances as short as 3.32 and 3.37 Å in [CpNi(bdt)] and [CpNi(bds)], while the angles between the Cp mean planes are 4.46 and 4.17° in [CpNi(bdt)] and [CpNi(bds)], respectively.

![Figure 8](image-url)  
Figure 8. Projection view along the \(b\) axis of the unit cell of [CpNi(bdt)].

![Figure 9](image-url)  
Figure 9. Temperature dependence of the magnetic susceptibility of [CpNi-(bdt)] (O) and [CpNi(bds)] (●). Solid lines are fits to the Bleaney–Bower singlet−triplet model with a Curie tail at the lowest temperatures (see text).

At this stage, we can tentatively conclude that the strong antiferromagnetic interaction observed in those complexes can be attributed to this original Cp•••Cp overlap. Taking this solid-state organization into account, we performed a fit of the susceptibility data with a singlet−triplet model, together with a contribution, observable at low temperatures, of a Curie-type susceptibility (Curie tail) attributable to paramagnetic defaults. The best fits afforded \(JK\) values of \(-402(4)\) \((279\ \text{cm}^{-1})\) and \(-451(6)\) K \((313\ \text{cm}^{-1})\), together with Curie contribution of 0.8 and 2.6% for the [CpNi(bdt)] and [CpNi(bds)] complexes, respectively. To strengthen this hypothesis, quantum calculations were performed on the [CpNi(bdt)] complex to obtain the shape of its SOMO, as well as the distribution of the spin density. The calculations were performed with the Gaussian03 code with the hybrid B3LYP functional. We have employed a triple-ζ all-electron Gaussian basis set for the nickel atoms and a double-ζ basis set for the other elements proposed by Schaefer et al. As shown in Figure 11, the SOMO is largely distributed on the dithiolate ligand and the nickel atom, as already observed for the SOMO of [CpNi(dmit)].

It is therefore expected that the antiferromagnetic interactions would be dominated by interactions between the dithiolate ligands when present. However, as shown in Table 5, Mulliken and NBO analysis of the spin distribution show that 40−42% of the spin density is delocalized on the nickel atom, 31−32% on the two chalcogen atoms, and a far from negligible 21% on the cyclopentadienyl ring. These results confirm that, in the absence of any intermolecular S•••S or Ni•••S interactions, the Cp•••Cp overlap observed in the X-ray crystal structure of [CpNi(bdt)] can indeed justify the strong antiferromagnetic interaction experimentally deduced from the temperature dependence of the magnetic susceptibility.
Similar calculations performed on the [CpNi(dddt)] complex shows also a large delocalization of the SOMO, and as shown in Figure 12, the spin density is largely delocalized on the whole metallacycle with only 12% left on the Cp ring. These observations justify a posteriori the assumption made above that the strongest intermolecular interactions in [CpNi(dddt)] were essentially attributable to S⋯S contacts. They also give us some insight about the probable differences between the two classes of complexes which were identified above. Indeed, while both [CpNi(bdt)] and [CpNi(dddt)] appeared to fit nicely in the well-established electrochemical series known for square-planar bis(dithiolene) complexes with S2C2Me2 > S2C2Ph2 > dddt ≈ bdt > dmit > mnt, the much lower energy absorption band (1000 nm) observed only in [CpNi(dddt)] and [CpNi(dmit)] identify those two complexes as peculiar in the series, but it is at a particularly low energy (1000 nm) in the dddt and dmit complexes (and selenated analogues) when compared with S2C2Me2, S2C2Ph2, bdt, or mnt complexes, where it is observed between 750 and 800 nm. Finally, an original intermolecular Cp⋯Cp σ overlap has been identified in the solid state structure of [CpNi(bdt)] and [CpNi(bds)] as the only possible pathway for a strong antiferromagnetic interaction, which most probably finds its origin in a sizable spin density distribution of the cyclopentadienyl ring, a very original feature in organometallic radical complexes. Theoretical investigations are currently underway to (i) determine the origin of the NIR absorption of these complexes, particularly in [CpNi(dmit)] and [CpNi(dddt)], and (ii) to quantitatively evaluate the magnetic coupling constants.51

### Conclusion

The investigation of novel synthetic procedures for the preparation of these [CpNi(dt)] series has shown that the partially oxidized dithiolene complexes [Ni(dt)2]2+ react not only with the air-sensitive NiIII [Cp2Ni]BF4 species, as observed earlier,11,12 but also, in good yields, with the air stable NiII [CpNi(cod)]BF4 complex, providing a very efficient route particularly adapted to electron-poor dithiolate ligands available as [Ni(dt)2]2− anions. On the other hand, the oxidized [Ni(dt)2]0 complexes were shown to react not only with the NiII [Cp2Ni] complex12 but also with the NiI [CpNi(CO)]2 dimer with comparable and good yields. A strong NIR absorption band is observed in all complexes, but it is at a particularly low energy (1000 nm) in the dddt and dmit complexes (and selenated analogues) when compared with S2C2Me2, S2C2Ph2, bdt, or mnt complexes, where it is observed between 750 and 800 nm. Finally, an original intermolecular Cp⋯Cp σ overlap has been identified in the solid state structure of [CpNi(bdt)] and [CpNi(bds)] as the only possible pathway for a strong antiferromagnetic interaction, which most probably finds its origin in a sizable spin density distribution of the cyclopentadienyl ring, a very original feature in organometallic radical complexes. Theoretical investigations are currently underway to (i) determine the origin of the NIR absorption of these complexes, particularly in [CpNi(dmit)] and [CpNi(dddt)], and (ii) to quantitatively evaluate the magnetic coupling constants.51

### Experimental Section

**General Remarks.** All reactions were carried out under an argon atmosphere by means of standard Schlenk techniques. All solvents for chemical reactions were dried and distilled by Na benzophenone (for toluene) or CaH2 (for methanol) before use. The square-planar
and \([\text{CpNi(cod)}](\text{BF}_4)\) were prepared by literature methods. \([\text{Cp}_2\text{Ni}(\text{dithiolene})]\), \([\text{Ni(dddt)}_2]\), \([\text{Ni(ddds)}_2]\), \([\text{Ni(dsdt)}_2]\), \([\text{Ni(bdt)}_2]\) and \([\text{Ni(bds)}_2]\) were synthesized by literature methods. \(\text{O}_2\) and \([\text{CpNi(CO)}]_2\) were obtained from STREM Chemicals and Aldrich Chemicals, respectively. Silica gel (Silica gel 60) was obtained from MERCK, Ltd. The TOF-mass spectrum was recorded on a Bruker Daltonics MALDI-TOF BIFLEX III mass spectrometer. UV-vis and NIR spectra were recorded on Hitachi Model UV-2500PC and PERKIN ELMER Model Lambda 19 UV/VIS/NIR spectrometers, respectively. Elemental analyses were performed by the “Service d’Analyse du CNRS” at Gif/Yvette, France. UV irradiation for a photoreaction was performed with a high-pressure Hg lamp (Applied Photophysics, Ltd).

Reactions of \([\text{Cp}_2\text{Ni}]\) or \([\text{CpNi(CO)}]_2\) with the Neutral Square-Planar Nickel Dithiolene and Diselenolene Complexes. A toluene solution (50 mL) of \([\text{Cp}_2\text{Ni}]\) (38 mg, 0.2 mmol) and the square-planar dithiolene complexes \([\text{Ni(dithiolene)}_2]\) (dithiolene = dddt, ddds, bdtd, and bds; 0.2 mmol) was reacted at 80 °C for 2 h. After the solvent was removed under reduced pressure, the residue was separated by a column chromatography (silica gel, dichloromethane/n-hexane = 1:1 (v/v)). The product was further purified by recrystallization (n-hexane/dichloromethane). \([\text{CpNi(dddt)}]\) was obtained in a 59% yield. \([\text{CpNi(cod)}](\text{BF}_4)\) (64 mg, 0.2 mmol) reacted with \((\text{NBu}_4)_2[\text{Ni(dddt)}_2]\) (132 mg, 0.2 mmol) to give \([\text{CpNi(dddt)}]\) in an 86% yield.

**Thermal Reactions of \([\text{Cp}_2\text{Ni}]\) or \([\text{CpNi(CO)}]_2\) with \(\text{O}_2\).**

A solution of \([\text{Cp}_2\text{Ni}]\) (94 mg, 0.5 mmol) and \(\text{O}_2\) (94 mg, 0.5 mmol) was reacted in refluxing toluene for 24 h. After the reaction, silica gel was added to the reaction mixture, and then, the remaining \([\text{Cp}_2\text{Ni}]\) was rapidly oxidized and adsorbed onto the silica gel. The mixture was separated by column chromatography (silica gel, dichloromethane/n-hexane = 1:1 (v/v)). The black solid of \([\text{CpNi(dddt)}]\) was obtained in a 29% yield. The thermal reaction of \([\text{CpNi(CO)}]_2\) (76 mg, 0.25 mmol) with \(\text{O}_2\) (104 mg, 0.5 mmol) was also performed, and \([\text{CpNi(dddt)}]\) was isolated in a 29% yield.

**Photoreactions of \([\text{Cp}_2\text{Ni}]\) or \([\text{CpNi(CO)}]_2\) with \(\text{O}_2\)**

A toluene solution (300 mL) of \([\text{Cp}_2\text{Ni}]\) (57 mg, 0.3 mmol, \(c = 1.0 \times 10^{-3}\) mol dm\(^{-3}\)) and \(\text{O}_2\) (63 mg, 0.3 mmol, \(c = 1.0 \times 10^{-3}\) mol dm\(^{-3}\)) was reacted for 24 h by using UV irradiation from a high-pressure Hg lamp (400 W). After the reaction, a black precipitate was filtered off, and the filtrate was evaporated under reduced pressure. The residue was separated by a column chromatography (silica gel, dichloromethane/n-hexane = 1:1 (v/v)).

**Table 6. Crystallographic Data of \([\text{CpNi(dithiolene)}_2]\) and \([\text{CpNi(ddds)}_2]\) Complexes**

<table>
<thead>
<tr>
<th>Complex</th>
<th>(a_1) (Å)</th>
<th>(b_1) (Å)</th>
<th>(c_1) (Å)</th>
<th>(V_1) (Å(^3))</th>
<th>(R_1)</th>
<th>(R_1) (Refined)</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{CpNi(dddt)}_2])</td>
<td>9.1045(8)</td>
<td>9.2000(8)</td>
<td>6.2605(10)</td>
<td>2256.8(4)</td>
<td>1.0</td>
<td>0.40</td>
</tr>
<tr>
<td>([\text{CpNi(ddds)}_2])</td>
<td>10.54(19)(10)</td>
<td>10.823(10)</td>
<td>3797.91</td>
<td>13249.8(4)</td>
<td>0.54</td>
<td>0.24</td>
</tr>
</tbody>
</table>
1:1 (v/v)). [CpNi(dddt)] was obtained in a 28% yield. [CpNi] or [CpNi(cood)](BF₄) in the same condition noted above.

[CpNi(dddt)], TOF-Mass (MALDI, 19 kV): m/z 303 (M⁺), 275 (M⁺ - (CH₂)₂), UV−vis−NIR (CH₂Cl₂, λmax (ε)): 1012 (4700), 417 (4600), 329 (24 000), 270 nm (14 000). Anal. Calcd for C₉H₉NiS₂: C, 35.54; H, 2.98; S, 42.17. Found: C, 35.64; H, 3.17; N, 42.12.

[CpNi(ddds)], TOF-Mass (MALDI, 19 kV): m/z 399 (M⁺(80Se)), 371 (M⁺(80Se) - (CH₂)₂), UV−vis−NIR (CH₂Cl₂, λmax (ε)): 1000 (3600), 395 (1800), 339 (23 000), 270 nm (15 000). Anal. Calcd for C₉H₀NiS₂Se₂: C, 27.17; H, 2.28; S, 16.12. Found: C, 27.33; H, 2.46; S, 16.22.

Crystallographic data of complexes are summarized in Table 6. Hydrogen atoms were introduced at calculated positions (riding model), least-squares methods. Absorption corrections were applied. Hydride measurements were performed on a Quantum Design MPMS-2 SQUID magnetometer operating on the range of 2−300 K at 5000 G with polycrystalline samples of [CpNi(dddt)] (17.88 mg), [CpNi(ddds)] (9.53 mg), [CpNi(ddsd)] (8.14 mg), [CpNi(bdt)] (19.73 mg), and [CpNi(bds)] (58.4 mg). Gelatin capsules were used with polycrystalline samples of [CpNi(dddt)] (17.88 mg), [CpNi(ddds)] (9.53 mg), [CpNi(ddsd)] (8.14 mg), [CpNi(bdt)] (19.73 mg), and [CpNi(bds)] (58.4 mg). Gelatin capsules were used with polycrystalline samples of [CpNi(dddt)] (17.88 mg), [CpNi(ddds)] (9.53 mg), [CpNi(ddsd)] (8.14 mg), [CpNi(bdt)] (19.73 mg), and [CpNi(bds)] (58.4 mg).

EPR Measurements. The preparations of sample solutions for EPR measurements were carried out in a drybox: 1.0 mmol dm⁻³ dichloromethane solutions of complexes were prepared, except for the solution of [CpNi(dddt)], which was prepared in toluene solution. The EPR spectra were recorded on a Bruker ESP 300 spectrometer (X-band), except for that of [CpNi(ddsd)], which was investigated on a Bruker EMX EPR spectrometer (X-band).

Magnetic Susceptibility Measurements. Magnetic susceptibility measurements were performed on a Quantum Design MPMS-2 SQUID magnetometer operating on the range of 2−300 K at 5000 G with polycrystalline samples of [CpNi(dddt)] (17.88 mg), [CpNi(ddds)] (9.53 mg), [CpNi(ddsd)] (8.14 mg), [CpNi(bdt)] (19.73 mg), and [CpNi(bds)] (58.4 mg). Gelatin capsules were used with a magnetization contribution of −2.37 × 10⁻⁶ + (2.2 × 10⁻⁶/T + 2) emu G⁻¹ which was used for correction of the experimental magnetization. Molar susceptibilities were then corrected for Pascal diamagnetism. Fits to the alternated chain model are based on the following expression (eq 1) of the spin Hamiltonian for an alternated chain, −A₂i−1 − (J) − A₂i − (αJ) − A₂i+1, while the susceptibility of the [CpNi(bdt)] and [CpNi(bds)] complexes was fitted with eq 2 where x is the fraction of S = 1/2 magnetic defaults

\[
H = -J \sum [S_{i} S_{i+1} + \alpha S_{i} S_{i+1}] \\
\chi = (1 - x) \frac{N g^2 \beta^2}{kT[3 + \exp(-J/kT)]} + x \frac{N g^2 \beta^2}{2kT}
\]

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Supporting Information Available: CIF files giving crystallographic data for [CpNi(dddt)], [CpNi(ddds)], [CpNi(ddsd)], [CpNi(bdt)], and [CpNi(bds)], tables of bond distances and angles, and a figure for the cyclic voltammetry. This material is available free of charge via the Internet at http://pubs.acs.org.