

## Strong Magnetic Interactions through Weak Bonding Interactions in Organometallic Radicals: Combined Experimental and Theoretical Study

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**Abstract:** The magnetic properties of a series of three neutral radical organometallic complexes of general formula [CpNi(dithiolene)]<sup>•</sup> have been investigated by a combination of X-ray crystal structure analysis and magnetic susceptibility measurements, while the assignment of the exchange coupling constants to the possible exchange pathways has been accomplished with the help of calculations based on density functional theory (DFT). The syntheses and X-ray structures of [CpNi(adt)] (adt = acrylonitrile-2,3-dithiolate) and

[CpNi(tfd)] (tfd = 1,2-bis(trifluoromethyl)ethene-1,2-dithiolate) complexes are described, while [CpNi(mnt)] (mnt = maleonitriledithiolate) was reported earlier. In the three complexes, we observed strong antiferromagnetic coupling that could not be explained solely by short S...S intermolecular con-

tacts. Our calculations indicated that spin density in these complexes is strongly delocalized on the NiS<sub>2</sub> moiety, with up to 20% on the Cp ring. As a consequence, Cp...Cp and Cp...dithiolene overlap interactions have been identified as responsible for antiferromagnetic couplings. The [CpNi(adt)] complex thus has a value  $J = -369.5 \text{ cm}^{-1}$  for an exchange interaction through a  $\pi$  stacking due to the Cp...Cp overlap.

**Keywords:** antiferromagnetism • density functional calculations • exchange interactions • organometallic radicals • pi stacking

### Introduction

In the field of molecular magnetism, the presence of bridging ligands between metallic paramagnetic centers plays a fundamental role in governing the strengths and natures of the magnetic interactions.<sup>[1,2]</sup> Despite the considerable prog-

ress achieved so far, one of the main problems in this field is due to the fact that many bridging ligands provide only weak magnetic exchange interactions although they are strongly coordinated to the metal atoms. The presence of weakly bonding interactions such as hydrogen bonds,  $\pi$  stacking or van der Waals forces in the exchange pathway usually results either in very weak (in most cases) or at best moderate magnetic interactions. Hence, new systems showing relatively large exchange coupling constants through weak interactions would open a wide range of possibilities for the design of improved metal-based molecular magnets.

From the theoretical point of view, calculations of the exchange couplings between paramagnetic centers, as well as good quantitative estimates of the coupling constants, are now becoming affordable even for very large systems through the use of density functional theory methods,<sup>[3,4]</sup> or for simpler systems by use of the difference dedicated configuration interaction approach.<sup>[5]</sup> This kind of study is crucial for understanding the magnetic properties, because in many cases it is difficult to interpret the experimental measurements. This is especially true for the study of systems with many paramagnetic centers,<sup>[6]</sup> because the fitting procedures or the magnetic susceptibility cannot be employed in, for instance, molecules showing slow relaxation of the mag-

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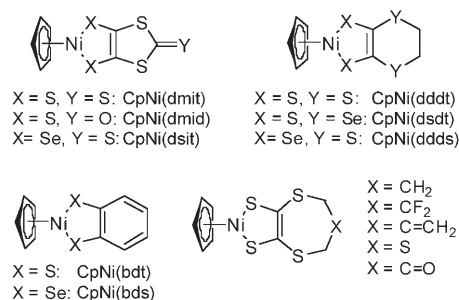
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netization, usually known as Single Molecule Magnets (SMMs).<sup>[7,8]</sup>

Another research field in which magnetic properties are in many cases not easily understood involves those compounds in which the spin density is not essentially localized on metal d orbitals. Such organic systems have been investigated in the search for organic ferromagnetism, and neutral radicals such as nitroxide-,<sup>[9]</sup> aminoxyl-,<sup>[10]</sup> or triarylmethyl-based<sup>[11]</sup> molecules have found most applications, either as materials in their own right or in combination with paramagnetic metals. Other related radical species derived from donor (decamethylferricinium, TTF<sup>+</sup>) or acceptor (TCNE<sup>-</sup>, TCNQ<sup>-</sup>) molecules, as well as radical square-planar bis(dithiolene) complexes [Ni(dmit)<sub>2</sub><sup>-</sup>, Ni(tfd)<sub>2</sub><sup>-</sup>, Ni(mnt)<sub>2</sub><sup>-</sup>] (dmit = 2-thioxo-1,3-dithiole-4,5-dithiolate, tfd = 1,2-bis(trifluoromethyl)ethene-1,2-dithiolate, mnt = maleonitriledithiolate) have also been extensively investigated in the solid state for their magnetic properties, since the ferro- or antiferromagnetic interactions that characterize most of these compounds can develop into isolated dyads with singlet-triplet behavior, or into one-, two-, or three-dimensional magnetic networks.<sup>[12]</sup> This ability to adopt periodic structures and the presence of weak intermolecular interactions allows for the observation of some physical behavior that cannot be presented by the usually studied paramagnetic transition metal complexes. Several molecular Heisenberg uniform chain systems based on tetrathiafulvalene salts, for instance, have recently been described.<sup>[13–15]</sup> Such 1D systems can be also affected by a spin-Peierls transition,<sup>[16]</sup> an issue of current strong interest in the solid-state physics community for its characteristic magnetic field/temperature (*H/T*) phase di-

agram.<sup>[17,18]</sup> Spin ladder systems have also recently been observed in molecular systems based variously on tetrathiafulvalene derivatives,<sup>[19,20]</sup> square-planar bis(dithiolene) complexes,<sup>[21]</sup> or organometallic, formally d<sup>1</sup>, Cp<sub>2</sub>M(dithiolene)<sup>+</sup> complexes (M = Mo, W).<sup>[22,23]</sup> Three-dimensionally ordered antiferromagnets, based either on tetrathiafulvalenium salts with antiperovskite structures,<sup>[24]</sup> or on organometallic heteroleptic complexes associating both cyclopentadienyl and dithiolene complexes,<sup>[25]</sup> have also been described. The latter class of antiferromagnets includes complexes such as Cp<sub>2</sub>M(dithiolene)<sup>+</sup> salts (M = Mo, W),<sup>[26–28]</sup> the neutral S = 1/2—formally d<sup>1</sup>—[Cp<sup>\*</sup>M(dmit)<sub>2</sub>]<sup>•</sup> (M = Mo, W),<sup>[29,30]</sup> or the formally d<sup>7</sup>, S = 1/2 [CpNi(dmit)]<sup>•</sup> complexes.<sup>[31,32]</sup> We have already investigated a wide variety of such [CpNi(dithiolene)]<sup>•</sup> complexes, in which the dithiolene moiety is fused variously with a five-membered ring, as in [CpNi(dmit)], a six-membered ring,<sup>[33]</sup> as in [CpNi(dddt)] (dddt = 5,6-dihydro-1,4-dithiine), or a seven-membered ring,<sup>[34]</sup> with various outer substituents. They are all characterized—except for [CpNi(bdt)]



**Abstract in French:** *Les propriétés magnétiques d'une série de trois complexes neutres organométalliques radicalaires de formule générale [CpNi(dithiolène)]<sup>•</sup> sont étudiées par une analyse conjointe de leurs structures déterminées par diffraction des RX et de mesures de susceptibilité magnétique, tandis que l'attribution des constantes de couplage d'échange aux différents chemins d'échange possibles a été réalisée avec l'aide de calculs basés sur la théorie de la fonctionnelle de densité (DFT). Les synthèses et les structures aux rayons X des complexes [CpNi(adt)] (adt = acrylonitrile-2,3-dithiolate) et [CpNi(tfd)] (tfd = trifluorométhyléthène-1,2-dithiolate) sont décrites ici, alors que le complexe [CpNi(mnt)] (mnt = maleonitriledithiolate) a été publié antérieurement. Dans les trois complexes, nous avons observé un fort couplage antiferromagnétique qui ne peut pas être seulement expliqué par les courts contacts intermoléculaires S...S. Nos calculs ont indiqué que la densité de spin dans ces complexes est fortement délocalisée sur la partie NiS<sub>2</sub>, avec jusqu'à 20 % sur le cycle C<sub>p</sub>. Par conséquent, les interactions Cp...Cp et Cp...dithiolène sont identifiées comme étant également responsables des couplages antiferromagnétiques. Ainsi, le complexe [CpNi(adt)] a une valeur de  $J = -369.5 \text{ cm}^{-1}$  pour une interaction d'échange de type  $\pi$ - $\pi$  dû au recouvrement Cp...Cp.*

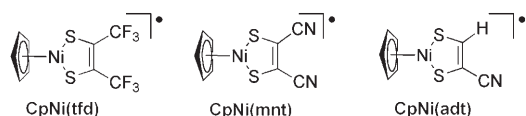
(bdt = 1,2-benzenedithiolate)—by large numbers of sulfur atoms, which favor strong intermolecular interactions in the solid state, leading variously to three-dimensional antiferromagnetic ground states or to one-dimensional (possibly alternating) spin chains or dimeric entities with singlet ground states.

As stated above, it is highly desirable to investigate whether the theoretical approaches based on density functional theory, used up to now for evaluating the exchange coupling interactions between metallic spins essentially localized in d orbitals in a quantitative way, can also be applied to molecular organic or organometallic systems in which the spin density is now strongly delocalized on molecular s or p orbitals. In that respect, these neutral radical species of general formula [CpNi(dithiolene)]<sup>•</sup> offer an excellent foundation to test these calculations as: i) the spin density is delocalized on the nickel and both Cp and dithiolene ligands, ii) the role of the  $\pi$  stacking in the exchange interaction between molecules can be examined, and iii) the absence of any counterion limits the possible interaction paths to direct exchange interactions only.

Investigation of the magnetic behavior of these complexes, as in most molecular materials based on the temper-

ature dependence of their magnetic susceptibility, has so far essentially been based on structural analysis of so-called “short” S⋯S intermolecular contacts, with most of the spin density being considered to be located on the sulfur atoms of the NiS<sub>2</sub>C<sub>2</sub> metallacycle. This approach has shown its limitations: in [CpNi(bdt)],<sup>[33]</sup> for example, we found that the observed singlet–triplet behavior could only be attributed to a face-to-face Cp⋯Cp overlap, on the basis of the absence of any other short contact and the observation of a non-negligible spin density of the Cp moiety in [CpNi(bdt)].

Among the numerous [CpNi(dithiolene)] complexes currently available for these theoretical studies, we have concentrated our attention on some of the simplest, such as [CpNi(tfd)], [CpNi(mnt)], and [CpNi(adt)] (adt = acrylonitrile-2,3-dithiolate) complexes. Indeed, as shown below,



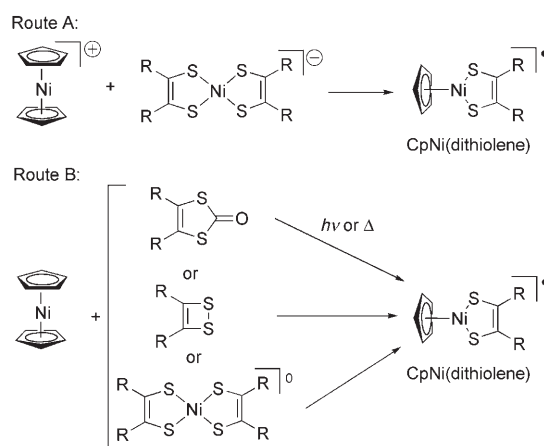
those radical species can interact with each other through a combination of different intermolecular  $\sigma$  and  $\pi$  overlaps between the dithiolene and the cyclopentadienyl moieties.

They therefore offer a magnificent arena in which to evaluate the adaptability of the theoretical calculations described above in the different overlap situations, which can be encountered in all molecular paramagnetic molecular solids exhibiting intermolecular interactions. This encompasses not only many magnetic semiconducting or insulating tetrathiafulvalene salts and all radical dithiolene complexes,<sup>[35,36]</sup> but also the well known neutral radicals: in the phenalenyl<sup>[37–39]</sup> and in the thiazolyl<sup>[40,41]</sup> series, for example.

In this work we describe original syntheses and X-ray crystal structures of [CpNi(tfd)] and [CpNi(adt)] and investigate the relationship between the solid-state structures of the three [CpNi(tfd)], [CpNi(mnt)], and [CpNi(adt)] complexes and the temperature dependence of their magnetic behavior, in the light of calculated exchange interaction constants ( $J$ ) based on density functional theory, specifically applied here to molecular organometallic systems with highly delocalized spin densities.

## Results and Discussion

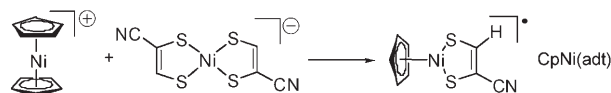
**Synthesis:** The described syntheses of these formally Ni<sup>III</sup> [CpNi(dithiolene)] complexes essentially follow two different routes (Scheme 1). Route A involves the reaction of two Ni<sup>II</sup> species: the square planar [Ni(dithiolene)<sub>2</sub>]<sup>−</sup> radical species with the nickelocene [Cp<sub>2</sub>Ni][BF<sub>4</sub>] salt, as previously reported for [CpNi(mnt)]<sup>[42]</sup> or [CpNi(dmit)].<sup>[31,32]</sup> Route B involves the reaction of a neutral, oxidized dithiolene precursor (such as a dithiete, a 1,3-dithiol-2-one, or a neutral [Ni(dithiolene)<sub>2</sub>]<sup>0</sup> complex), which oxidizes Ni<sup>II</sup> nickelocene to afford the expected, formally Ni<sup>III</sup>, [CpNi(dithio-



Scheme 1.

lene)] complex.<sup>[33,42]</sup> Our experience has showed that route A is better adapted to dithiolate ligands with electron-withdrawing substituents such as mnt or dmit, while route B requires either more electron-rich dithiolates—allowing the isolation of the corresponding dithiete or neutral [Ni(dithiolene)<sub>2</sub>]<sup>0</sup> species—or suitable thermal or photochemical reactivity of the corresponding 1,3-dithiol-2-one.

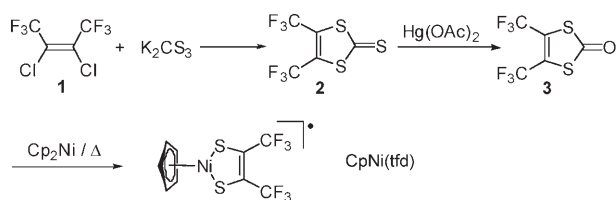
Accordingly, [CpNi(mnt)] was prepared by route A as previously described,<sup>[42]</sup> as the monoanionic [Ni(mnt)<sub>2</sub>]<sup>−</sup> is readily available. Similarly, the preparation of [CpNi(adt)] was successfully attempted by the same route, by treatment of [Cp<sub>2</sub>Ni][BF<sub>4</sub>] with [PPh<sub>4</sub>][Ni(adt)<sub>2</sub>] (Scheme 2).<sup>[43]</sup> The neutral radical was obtained in 32% yield and recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/pentane.



Scheme 2.

[CpNi(tfd)] had already been described 30 years ago<sup>[44]</sup> and its reported preparation involved the reaction between nickelocene and the (CF<sub>3</sub>)<sub>2</sub>C<sub>2</sub>S<sub>2</sub> dithiete (route B), itself obtained by treatment of the gaseous hexafluorobutylene with boiling sulfur.<sup>[45]</sup> We have recently reported<sup>[46]</sup> that the corresponding 1,3-dithiole-2-thione—that is, bis-4,5-(trifluoromethyl)-1,3-dithiole-2-thione (**2**)—could be obtained by a simpler method through the nucleophilic displacement of chlorine atoms in 1,1,1,4,4,4-hexafluoro-2,3-dichlorobut-2-ene (**1**) with potassium trithiocarbonate (K<sub>2</sub>CS<sub>3</sub>; Scheme 3). Oxymercuration of **2** with Hg(OAc)<sub>2</sub> in CHCl<sub>3</sub>/AcOH then affords the corresponding bis-4,5-(trifluoromethyl)-1,3-dithiol-2-one (**3**),<sup>[47]</sup> which reacts with nickelocene to give [CpNi(tfd)] in low yield after column chromatography and crystallization from CH<sub>2</sub>Cl<sub>2</sub>/pentane.

The three compounds are air-stable, crystalline solids. Cyclic voltammetry experiments performed in CH<sub>2</sub>Cl<sub>2</sub> (Table 1) showed that they reversibly oxidize to the cationic



Scheme 3.

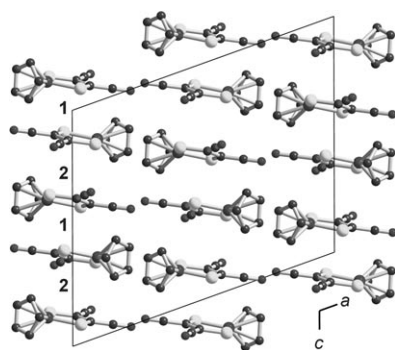
Table 1. CV data for the [CpNi(dithiolene)] complexes.

Compound	$E_{1/2}(-1 \rightarrow 0)$ [V] <sup>[a]</sup>	$E_{1/2}(0 \rightarrow +1)$ [V] <sup>[a]</sup>	$E_{\text{ox}} - E_{\text{red}}$	Ref.
[CpNi(mnt)] <sup>•</sup>	-0.64 <sup>[r]</sup>	+0.79 <sup>[ir]</sup>	1.43	[42]
[CpNi(tfd)] <sup>•</sup>	-0.80	+0.64	1.44	this work
[CpNi(adt)] <sup>•</sup>	-0.81	+0.52	1.33	this work

[a] In V vs. Fc<sup>+</sup>/Fc. [r] Reversible. [ir] Irreversible.

(formally d<sup>6</sup>) species and reversibly reduce to the anionic (formally d<sup>8</sup>) species, as observed in analogous complexes such as [CpNi(dmit)].<sup>[31,32]</sup>

**X-ray crystal structures:** While the structure of [CpNi(mnt)]<sup>•</sup> had been reported earlier, those of [CpNi(adt)]<sup>•</sup> and [CpNi(tfd)]<sup>•</sup> were determined here in order to interpret the magnetic behavior of these three radicals in terms of the solid-state structures they adopt. [CpNi(mnt)]<sup>•</sup> was found to crystallize in the monoclinic system, space group *C2/c* with one molecule in general position in the unit cell. In the solid state, the complexes organize into inversion-centered dyads through an interaction denoted (1) in Figure 1, with a plane-to-plane distance of 3.67 Å between the dithiolene moieties.

Figure 1. A projection view of [CpNi(mnt)] along *b*.

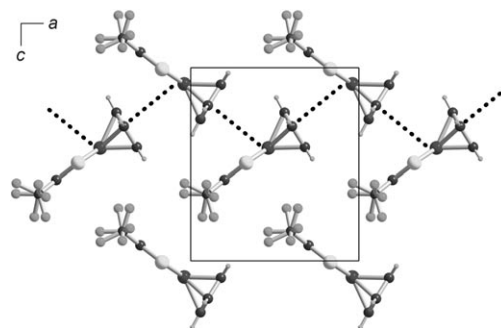
Those dyads establish short contacts with each other along the *c* axis, through interaction (2), as shown in Figure 1. No other short contacts between those columns are identified.

[CpNi(tfd)]<sup>•</sup> crystallizes in the orthorhombic system, space group *Pnma*, with one molecule located on a mirror plane incorporating the nickel atom and one carbon atom of the Cp ring. Note also that each fluorine atom of the CF<sub>3</sub> moiety is disordered between two positions. Important bond lengths and angles are listed in Table 2 for comparison with those of [CpNi(adt)]<sup>•</sup> and those reported for [CpNi(mnt)]<sup>•</sup>.

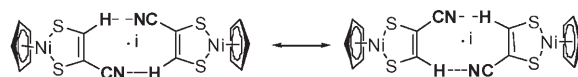
Table 2. Interatomic distances in the [CpNi(dithiolene)]<sup>•</sup> complexes.

Compound	Ni-S [Å]	S-C [Å]	C=C [Å]	Ref.
[CpNi(mnt)] <sup>•</sup>	2.1255(8) 2.1282(8)	1.715(3) 1.725(3)	1.354(4)	[42]
[CpNi(tfd)] <sup>•</sup>	2.1179(9)	1.731(3)	1.355(7)	this work
[CpNi(adt)] <sup>•</sup>	2.1167(17) 2.1225(15)	1.710(5) 1.691(6)	1.320(7)	this work

In the solid state, molecules are oriented perpendicular to each other into layers parallel to the (*a,c*) plane (Figure 2) with short intermolecular contacts only found between the Cp ring of one complex and the sulfur atom of a neighboring one along the *a* direction (C<sub>Cp</sub>...S: 3.767(5), 3.674(4) Å). In the *b* direction, molecules alternate in a head-to-tail fashion with the shortest intermolecular S...S contact at the long 4.249(1) Å distance, excluding any sizeable interaction along this direction.

Figure 2. A projection view of the (*a,c*) plane in [CpNi(tfd)]. The dotted lines indicate the magnetic interaction running along *a*.

The [CpNi(adt)]<sup>•</sup> complex crystallizes in the triclinic system, space group *P1̄* with one molecule in general position in the unit cell. The CN group is found to be disordered between two positions with equal occupation parameters. Each molecule is hydrogen bonded to a neighboring one through a CN...H-C interaction, giving rise in the crystal to a bimolecular cyclic motif shown in Scheme 4 and Figure 3.



Scheme 4.

Such a cyclic motif has already been observed in CN-containing molecules such as 1,4-dicyanobenzene<sup>[48]</sup> or 3-cyano-3',4'-ethylenedithiotetrathiafulvalene in its I<sub>3</sub><sup>-</sup> salt.<sup>[14]</sup> It has its origin in the activation of the hydrogen atom by the electron-withdrawing CN group located in the *ortho* position.<sup>[49]</sup>

A closer look at the structure reveals that any given complex, noted **Ni1** in Figure 4, has the potential to interact with four different neighbors: 1) through a Cp...Cp interaction, as the two Cp rings are parallel, with a short plane-to-

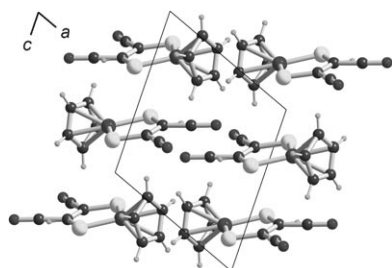


Figure 3. A projection view along *b* of the unit cell of [CpNi(adt)]. The two disordered positions of the  $\text{-CN}$  and  $\text{-H}$  groups have been shown.

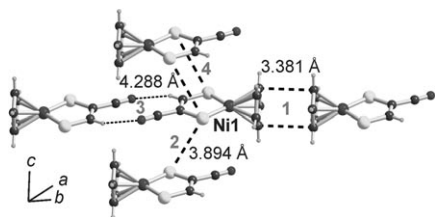


Figure 4. A detailed view of the four possible interactions (1–4) between one [CpNi(adt)] complex and its neighbors. Only one of the two disordered CN groups is shown for clarity.

plane distance of  $3.38 \text{ \AA}$ , 2) through a lateral  $\text{S}\cdots\text{S}$  contact at  $3.894 \text{ \AA}$ , 3) through the  $\text{C-H}\cdots\text{N}$  hydrogen-bonded motif described above, and finally, 4) in an inversion-centered dyad through two equivalent  $\text{S}\cdots\text{S}$  contacts at  $4.288 \text{ \AA}$ .

To summarize, the three radical complexes described above offer magnetic interactions of strikingly different natures: i) alternating chains running in the *c* direction in the structure of [CpNi(mnt)], characterized by a  $\sigma$  overlap between the  $\pi$  orbitals of the dithiolene fragments (Figure 1), ii) uniform chains running in the *a* direction in the structure of [CpNi(tfd)], through a novel  $\sigma$  overlap between the Cp and dithiolene fragments located perpendicular to each other (Figure 2), and iii) in [CpNi(adt)] (Figure 4), offering possibilities for  $\sigma$  overlap between face-to-face dithiolenes, lateral  $\pi$  overlap between dithiolenes, interaction through  $\text{C-H}\cdots\text{N}$  hydrogen bonding, or  $\pi$  stacking through a  $\text{Cp}\cdots\text{Cp}$  interaction.

**Magnetic properties in the solid state:** As shown in Figure 5, the temperature dependences of the magnetic susceptibilities of the three complexes exhibit very different behavior. Both [CpNi(mnt)] and [CpNi(adt)] are affected by strong antiferromagnetic interactions, with singlet ground states at low temperatures where Curie tails were detected in both compounds at low temperatures. The fits (solid lines) were obtained with a singlet–triplet (Bleaney–Bower) equation<sup>[50]</sup> with use of the Heisenberg Hamiltonian  $\hat{H} = -J\hat{S}_1\hat{S}_2$ . For clarity, we have removed the observed Curie tails, which correspond to magnetic impurities of  $S = 1/2$  species, of 0.8% for [CpNi(adt)] and 1.2% for [CpNi(mnt)]. Despite the problems of the fitting procedure, we can obtain a set of reasonable values:  $J = -369.5 \text{ cm}^{-1}$  and  $g = 2.01$  for [CpNi(adt)] and  $J = -236.7 \text{ cm}^{-1}$  and  $g = 2.04$  for [CpNi(mnt)],

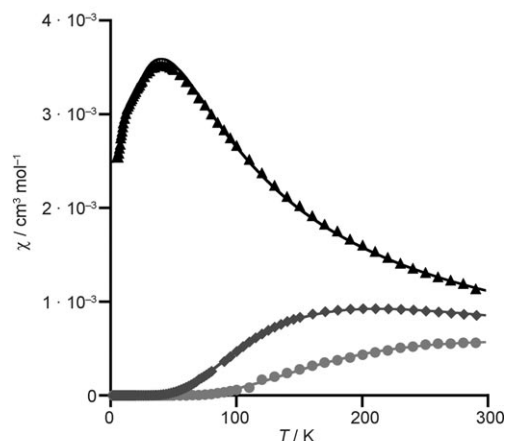


Figure 5. Temperature dependence of the magnetic susceptibilities of complexes [CpNi(tfd)] ( $\blacktriangle$ ), [CpNi(mnt)] ( $\blacklozenge$ ), and [CpNi(adt)] ( $\bullet$ ).

while a uniform chain model<sup>[51]</sup> (Bonner–Fisher) was employed for [CpNi(tfd)] to give  $J = -43.1 \text{ cm}^{-1}$  and  $g = 2.01$  with 3.5% of impurities of a regular chain.

**Theoretical study of magnetic coupling:** A short description of the methodology employed in this section has been included in the Computational Details. The more complicated situation is found in [CpNi(adt)], where four different possible interaction paths were identified (Figure 4). Calculations of exchange interactions afforded the following values:  $J_{\text{adt}} = -143.4 \text{ cm}^{-1}$  (1),  $J_{\text{adt}} = +5.8 \text{ cm}^{-1}$  (2),  $J_{\text{adt}} = -0.6 \text{ cm}^{-1}$  (3), and  $J_{\text{adt}} = +1.9 \text{ cm}^{-1}$  (4). It follows that the experimentally observed magnetic behavior in [CpNi(adt)], antiferromagnetic coupling with  $J = -369.5 \text{ cm}^{-1}$ , is exclusively attributable to one of the interactions (1): that is, the  $\pi$  stacking between cyclopentadienyl moieties of the two radical species. This is all the more unexpected, as the interactions in such sulfur-rich radical dithiolene complexes are most often usually dominated by  $\text{S}\cdots\text{S}$  or  $\text{S}\cdots\text{Ni}$  interactions. The unambiguous results of the calculations on [CpNi(adt)] reported here demonstrate for the first time that a strong antiferromagnetic interaction can be produced through  $\pi$  stacking due to the  $\text{Cp}\cdots\text{Cp}$  overlap. It is worth noting the considerable strength of the exchange interaction due to the weak interaction caused by the  $\pi$  stacking of the Cp rings.

The orbitals bearing the unpaired electrons are plotted in Figure 6; analysis of such orbitals reveals the presence of a large contribution from the carbon atoms of the dithiolene ligands in the SOMOs. However, such a contribution does not appear to be reflected in the total spin density. The large spin polarization of the doubly occupied orbitals gives considerably different  $\alpha$  and  $\beta$  orbitals, resulting in a total spin density with small contributions on the carbon atoms. Hence, the two empty  $\beta$  orbitals corresponding to the SOMOs (called UMOS;<sup>[52]</sup> see Figure 6b) provide a better picture of the spin density distribution than the equivalent  $\alpha$  occupied orbitals. This effect is not always as dramatic as shown for the [CpNi(adt)]; thus, for the [Ni(adt)<sub>2</sub>] complex

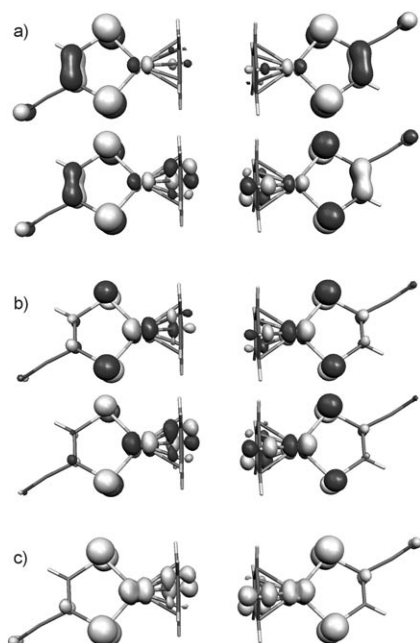


Figure 6. Representation of the two  $\alpha$  SOMOs (a), and relative  $\beta$  UM-SOs (b) and spin density distribution for a bimolecular model of the  $[\text{CpNi}(\text{adt})]$  compound (c). The isodensity surface represented corresponds to a value of  $0.005 \text{ e}^- \text{ bohr}^{-3}$ .

the differences between  $\alpha$  and  $\beta$  orbitals are smaller (see Figure S1, Supporting Information). For the  $[\text{CpNi}(\text{adt})]$ , we can see that spin density is very delocalized between the sulfur atoms and the Cp ring (see spin population values in Table 3).

Table 3. Spin populations with Mulliken and NBO analysis for the complexes  $[\text{CpNi}(\text{S}_2\text{C}_2\text{RR}')]^{\cdot}$  with  $\text{R}=\text{R}'=\text{CN}$  in  $[\text{CpNi}(\text{mnt})]$ ,  $\text{R}=\text{R}'=\text{CF}_3$  in  $[\text{CpNi}(\text{tfd})]$  and  $\text{R}=\text{CN}$ ,  $\text{R}'=\text{H}$  in  $[\text{CpNi}(\text{adt})]$ .

	$[\text{CpNi}(\text{adt})]$		$[\text{CpNi}(\text{mnt})]$		$[\text{CpNi}(\text{tfd})]$	
	Mulliken	NBO	Mulliken	NBO	Mulliken	NBO
Cp	0.21	0.22	0.21	0.23	0.23	0.24
Ni	0.38	0.36	0.43	0.40	0.41	0.39
S <sub>2</sub>	0.36	0.36	0.34	0.34	0.34	0.34
C=C	0.04	0.04	0.02	0.02	0.03	0.03
RR'	0.01	0.02	0.00	0.01	0.00	0.00

The large difference between the calculated and the experimentally determined values of the  $J_{\text{adt}}$  exchange interaction corresponding to the Cp...Cp interaction ("1" in Figure 4) let us infer that the compound might exhibit a variable exchange interaction upon temperature lowering. In order to test this assumption, further X-ray data collection was performed on  $[\text{CpNi}(\text{adt})]$  at 100 K, revealing that the compound had indeed undergone a structural transition. At 100 K,  $[\text{CpNi}(\text{adt})]$  crystallizes in the triclinic system, space group  $P\bar{1}$  with two crystallographically independent molecules in the unit cell, noted **Ni1** and **Ni2** below. As shown in Figure 7, the main features observed at room temperature are conserved, but the dyadic motifs linked by C–H...NC hydrogen bonds are now observed in homo-dyads **Ni1**...**Ni1**

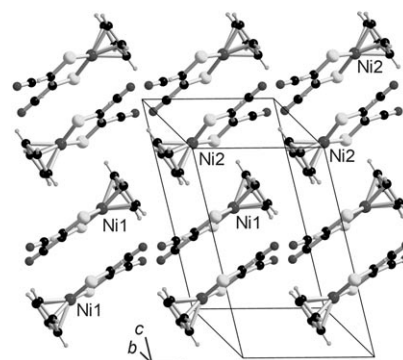


Figure 7. A view of one molecular plane in  $[\text{CpNi}(\text{adt})]$  at 100 K. The CN moieties disordered on both carbon atoms of the  $\text{NiS}_2\text{C}_2$  metallacycle are shown.

and **Ni2**...**Ni2**, while the Cp...Cp interaction correlates both independent complexes **Ni1** and **Ni2**. An important difference between the room temperature and the 100 K crystal structures is to be found in the details of this Cp...Cp interaction. Indeed, as a consequence of the rotation of one complex relative to the other in the low-temperature phase (Figure 8), the interacting cyclopentadienyl rings are now

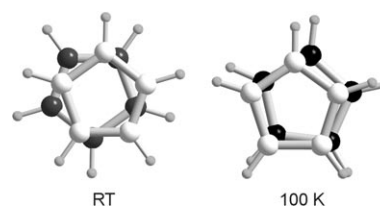


Figure 8. Detail of the Cp overlap in the RT and 100 K crystal structures of  $[\text{CpNi}(\text{adt})]$ .

almost eclipsed, while their relative separation has also decreased, from  $3.38 \text{ \AA}$  at RT to  $3.27 \text{ \AA}$  at 100 K ( $-3.3\%$ ). Both features point to increased interaction at lower temperatures, thus explaining why, with a temperature-independent  $J_{\text{adt}}$  value, we don't obtain a perfect fit of the magnetic behavior of  $[\text{CpNi}(\text{adt})]$  (Figure 5). We therefore calculated  $J_{\text{adt}}$  for the interaction 1 through the Cp ligands in this low-temperature geometry and indeed reached a larger interaction, at  $-166.8 \text{ cm}^{-1}$ , but without fully recovering the gap with the experimentally determined value ( $-369.5 \text{ cm}^{-1}$ ).

For the  $[\text{CpNi}(\text{mnt})]$  complex, we calculated the exchange coupling constants relating to both interactions 1 and 2, identified in Figure 1 and shown in more detail in Figure 9. In the inversion-centered dyad (1), the calculated  $J_{\text{mnt}}$  amounts to  $+2.6 \text{ cm}^{-1}$ , while for the perpendicular interaction between crystallographically independent molecules (2), the calculated  $J_{\text{mnt}}$  amounts to  $-157 \text{ cm}^{-1}$ , to be compared to the experimental value  $J_{\text{mnt}} = -237 \text{ cm}^{-1}$ . Therefore, the origin of the much stronger interaction (2) is to be found in the details of the overlap between radical species, combined with the distribution of the spin density (see

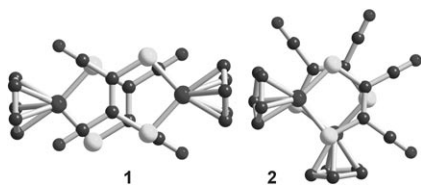


Figure 9. Details of the overlap interactions 1 and 2 along *c* in [CpNi(mnt)].

Table 3). As shown in Figure 9, interaction 1 involves two head-to-tail complexes in an inversion-centered dyad, with a relatively short plane-to-plane distance of 3.65 Å but long S...S (>4.27 Å) and no S...Ni contacts. The presence of short intermolecular distances between the carbon atoms of the dithiolene ligands does not result in a strong interaction, due to the small delocalization of the spin density in such atoms (see Figure 10). On the other hand, interaction 2 in-

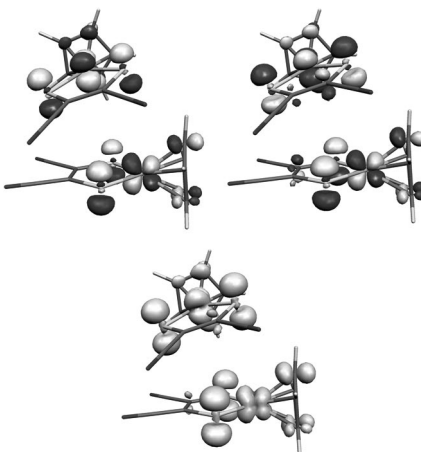


Figure 10. Representation of the two  $\beta$  UMSOs, and spin density distribution for a bimolecular model of the [CpNi(mnt)] compound. The isodensity surface represented corresponds to a value of  $0.005 e^- \text{ bohr}^{-3}$ .

volves dithiolene planes that are not fully parallel but have an almost eclipsed overlap between the metallacycles, together with two short Ni...S distances at 4.34 Å. Details of the spin density distribution in [CpNi(mnt)] (Figure 10) confirm this analysis, as it is essentially localized on the Ni and S atoms, together with a non-negligible part on the Cp ring (Table 3).

Let us now describe the third complex, which does not feature a Cp...Cp or dithiolene/dithiolene interaction but rather a highly unusual Cp...dithiolene interaction and the adoption of a regular chain structure. The exchange coupling constant relating to the shortest contact in the crystal of the [CpNi(tfd)] compound (Figure 11) was calculated for a dimeric entity and afforded  $J_{\text{tfd}} = -30 \text{ cm}^{-1}$ , to be compared with the experimentally determined value deduced from the fit of the magnetic behavior (Figure 5) with the Bonner–Fischer equation ( $J_{\text{tfd}} = -43.1 \text{ cm}^{-1}$ ). It demonstrates that the partial spin density delocalized on the Cp moiety



Figure 11. Detail of the overlap interaction within the [CpNi(tfd)] compound. Left: side view of interacting molecules. Right: Cp...dithiolene overlap.

(Table 3) in [CpNi(tfd)] might indeed interact in the solid state, here with the NiS<sub>2</sub>C<sub>2</sub> metallacycle, to afford a sizeable magnetic interaction (Figure 12).

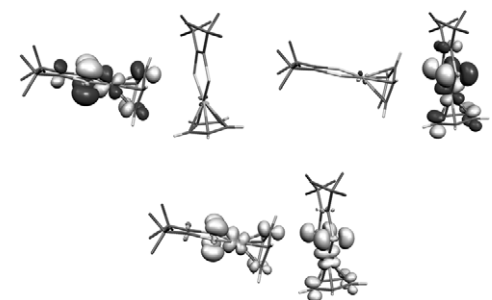


Figure 12. Representation of the two  $\beta$  UMSOs, and spin density distribution for a bimolecular model of [CpNi(tfd)]. The isodensity surface shown corresponds to a value of  $0.005 e^- \text{ bohr}^{-3}$ .

## Conclusions

As typical non-innocent ligands, radical dithiolene complexes are expected to develop a large part of their spin density on the dithiolate ligand. Up to now, it was considered that both the sulfur atoms and the carbon atoms have significant spin populations, due to spin delocalization. However, the analysis of the spin density has revealed that basically it is mainly localized on the sulfur and nickel atoms, with some contributions on the Cp rings. We have thus shown here, in this class of [CpNi(dithiolene)] neutral radical organometallic complexes, that this previously considered assumption was strongly misleading and that a sizeable part of the spin population (around 20%) was actually and unexpectedly delocalized onto the Cp ring. As a consequence, novel possibilities for strong intermolecular interactions between the radical species are now offered; these can involve either a Cp...Cp or a Cp...dithiolene interaction, as was observed experimentally in the [CpNi(adt)] and [CpNi(tfd)] complexes, respectively. It is thus worth noting that the [CpNi(adt)] complex shows a very strong antiferromagnetic interaction with  $J = -369.5 \text{ cm}^{-1}$  for an exchange coupling through  $\pi$  stacking due to the Cp...Cp overlap. The third [CpNi(mnt)] complex could be considered more “classical”, as the strongest intermolecular interactions involve dithiolene...dithiolene overlap. However, we have also unambiguously demonstrated that the origin of the strong antiferromagnetic interaction was not the inversion-centered

face-to-face dyad with a short interplanar distance (interaction **1**, Figure 9) but rather interaction **2**, which involves two noncoplanar dithiolates related to each other by a twofold axis running along *b*.

## Experimental Section

**Synthesis:** All reagents are commercially available unless otherwise stated. Dry solvents were obtained by distillation as indicated: THF on Na/benzophenone, CH<sub>2</sub>Cl<sub>2</sub> on P<sub>2</sub>O<sub>5</sub>, and MeOH on Mg. Nuclear magnetic resonance spectra were recorded at 500.04 MHz for <sup>1</sup>H, 125.75 MHz for <sup>13</sup>C, and 470.282 MHz for <sup>19</sup>F. Compound **2**,<sup>[46]</sup> [CpNi(mnt)],<sup>[42]</sup> (Cp<sub>2</sub>Ni)(BF<sub>4</sub>)<sup>[53]</sup> and [PPh<sub>4</sub>][Ni(adt)<sub>2</sub>]<sup>[43]</sup> were prepared as previously described.

**4,5-Bis(trifluoromethyl)-1,3-dithiol-2-one (3):** Thione **2** (14.9 g, 0.055 mol) and Hg(OAc)<sub>2</sub> (35.14 g, 0.11 mol) were stirred under nitrogen for 3.5 h in CHCl<sub>3</sub>/CH<sub>3</sub>CO<sub>2</sub>H 3:1 (400 mL). The white precipitate was filtered on Celite and washed with CH<sub>2</sub>Cl<sub>2</sub> (3 × 150 mL). Organic solvents were concentrated to 250 mL and washed with saturated NaHCO<sub>3</sub> and then water. After drying over MgSO<sub>4</sub> and removal of the solvents, the crude product was chromatographed on silica gel with pentane elution to yield **3** as a pale yellow oil (9.1 g, 65%). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ = 182.47 (s), 126.8 (q, <sup>2</sup>J<sub>C,F</sub> = 42.22 Hz), 118.45 (q, <sup>1</sup>J<sub>C,F</sub> = 276.38 Hz) ppm; <sup>19</sup>F NMR (CDCl<sub>3</sub>): δ = -55.46 ppm (s).

**[CpNi(tfd)]:** [CpNi(CO)]<sub>2</sub> (0.12 g, 0.39 mmol) and bis(trifluoromethyl)-1,3-dithiol-2-one (**3**, 0.2 g, 0.79 mmol) were heated at 80 °C under nitrogen in dry toluene (5 mL) for 2 h. The resulting green solution was evaporated. Chromatography on silica gel with pentane elution, followed by a dichloromethane/pentane 1:1 mixture, yielded [CpNi(tfd)] (16 mg, 5.9%) as black hexagonal plates after slow evaporation of the green fraction. Elemental analysis (%) calcd for C<sub>9</sub>H<sub>5</sub>F<sub>6</sub>NiS<sub>2</sub>: C 30.89, H 1.44; found: C 31.55, H 1.55.

**[CpNi(adt)]:** A solution of (Cp<sub>2</sub>Ni)(BF<sub>4</sub>) (100 mg, 0.363 mmol) in CH<sub>3</sub>CN (50 mL) was treated with a solution of [PPh<sub>4</sub>][Ni(adt)<sub>2</sub>] (230 mg, 0.37 mmol) in CH<sub>3</sub>CN (10 mL). The solution was stirred for 3 h and concentrated under vacuum, and the residue was chromatographed on silica gel with CH<sub>2</sub>Cl<sub>2</sub> elution. The concentrated green fraction was layered with pentane to afford [CpNi(adt)] as dark green crystals (27.5 mg, 32%). IR (KBr):  $\tilde{\nu}$  = 3099 (Cp C–H), 3032 (C–H), 2204 cm<sup>-1</sup> (C≡N); elemental analysis (%) calcd for C<sub>8</sub>H<sub>6</sub>NNiS<sub>2</sub>: C 40.21, H 2.53, N 5.86; found: C 40.15, H 2.45, N 5.90.

**Crystallographic data collection and structure determination:** Crystals were mounted on top of thin glass fibers. Data were collected with a Stoe Imaging Plate Diffraction System (IPDS) with use of graphite monochromated Mo-K $\alpha$  radiation ( $\lambda$  = 0.71073 Å). The crystal data are summarized in Table 4. Structures were solved by direct methods (SHELXS-97) and refined (SHELXL-97) by full-matrix, least-squares methods. Absorption corrections were applied for all structures. Hydrogen atoms were introduced at calculated positions (riding model), included in structure factor calculations, and not refined.

CCDC-633151 ([CpNi(adt)] at RT), -633152 ([CpNi(adt)] at 100 K), and -633150 ([CpNi(tfd)]) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif

**Magnetic measurements:** Magnetic susceptibility measurements were performed on a Quantum Design MPMS-2 SQUID magnetometer operating in the 2–300 K range at 5000 G with polycrystalline samples of the three [CpNi(dithiolene)] complexes. Gelatin capsules were used with a magnetization contribution of  $-2.37 \times 10^{-6} + (2.2 \times 10^{-6}/(T+2))$  emu G<sup>-1</sup>, which was used for correction of the experimental magnetization. Molar susceptibilities were then corrected for Pascal diamagnetism.

**Computational details:** A detailed description of the computational strategy adopted in this work can be found elsewhere,<sup>[3,4,54]</sup> so we will only briefly sketch its most relevant aspects here. By use of a phenomenologi-

Table 4. Crystallographic data.

Compound	[CpNi(tfd)]	[CpNi(adt)] <sub>RT</sub>	[CpNi(adt)] <sub>LT</sub>
formula	C <sub>9</sub> H <sub>5</sub> F <sub>6</sub> NiS <sub>2</sub>	C <sub>8</sub> H <sub>6</sub> NNiS <sub>2</sub>	C <sub>8</sub> H <sub>6</sub> NNiS <sub>2</sub>
<i>F</i> <sub>w</sub>	349.96	238.97	238.97
cryst. syst.	orthorhombic	triclinic	triclinic
space group	<i>Pnma</i>	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> [Å]	9.1351(18)	7.973(2)	7.9558(10)
<i>b</i> [Å]	11.975(2)	8.039(2)	8.4884(11)
<i>c</i> [Å]	10.508(2)	8.646(2)	15.045(2)
$\alpha$ [°]	90.00	74.40(3)	94.126(16)
$\beta$ [°]	90.00	64.96(3)	99.434(15)
$\gamma$ [°]	90.00	69.49(3)	114.300(14)
<i>V</i> [Å <sup>3</sup> ]	1149.5(4)	465.5(2)	902.4(2)
<i>Z</i>	4	2	4
$\rho$ <sub>calcd</sub> [Mg m <sup>-3</sup> ]	2.022	1.705	2.149
diffract.	Stoe-IPDS	Stoe IPDS	Stoe IPDS
<i>T</i> [K]	150(2)	293(2)	100(2)
$\mu$ [mm <sup>-1</sup> ]	2.105	2.470	2.576
$\theta$ range [°]	2.58–25.90	2.63–26.02	2.67–25.91
meas. refls.	8268	4650	8693
indep. refls.	1158	1688	3247
<i>R</i> <sub>int</sub>	0.0572	0.0736	0.0910
<i>I</i> > 2 $\sigma$ ( <i>I</i> ) refls.	949	1028	2119
abs. corr.	multi scan	multi scan	multi scan
<i>T</i> <sub>max</sub> , <i>T</i> <sub>min</sub>	0.3690, 0.6256	0.7169, 0.7859	0.7161, 0.8959
refined par.	94	128	241
<i>R</i> ( <i>F</i> ), <i>I</i> > 2 $\sigma$ ( <i>I</i> )	0.0339	0.0387	0.0306
<i>wR</i> ( <i>F</i> <sup>2</sup> ), all	0.0871	0.0956	0.0659
$\Delta\rho$ (e Å <sup>-3</sup> )	-0.37, +0.42	-0.32, +0.40	-0.523, +0.622

cal Heisenberg Hamiltonian  $\hat{H} = -J\hat{S}_1\hat{S}_2$  to describe the exchange coupling in a dinuclear compound, where *J* is the coupling constant, and *S*<sub>1</sub> and *S*<sub>2</sub> the local spins on centers 1 and 2, respectively, the coupling constant *J* can be related to the energy difference between states with different spin multiplicity. In this study, each [CpNi(dithiolene)] monomer is considered to have a local spin *S*<sub>1</sub> = *S*<sub>2</sub> = 1/2, so we arrive at the following expression for *J*:

$$E_{LS} - E_{HS} = J \quad (1)$$

The calculation of *E*<sub>HS</sub> and *E*<sub>LS</sub> by quantum chemical methods is, however, not straightforward. The main problem arises when one wants to evaluate the energy for the low-spin, antiferromagnetic state. A single determinant for this state is not a proper wave function and it corresponds to a broken symmetry solution with energy *E*<sub>BS</sub>. In previous works we have shown that, when using DFT-based wavefunctions, a reasonable estimate of the energy corresponding to the low-spin state, *E*<sub>LS</sub>, can be obtained directly from the energy of a broken-symmetry solution, *E*<sub>BS</sub>.<sup>[54–56]</sup> Experience has shown that the use of this equation gives good agreement with experimental data for a large variety of compounds with exchange-coupled electrons.<sup>[3,4,6,7]</sup> The hybrid, DFT-based B3LYP<sup>[57]</sup> method has been used in all calculations as implemented in the Gaussian 03 package.<sup>[58]</sup> The starting wave-functions were generated by use of the Jaguar package.<sup>[59]</sup> As we treat non-innocent ligands, we used a large basis set proposed by Weigend et al.<sup>[60]</sup> of quadruple- $\zeta$  quality for the transition metal atoms, triple- $\zeta$  quality for sulfur and carbon atoms, and finally double- $\zeta$  quality for hydrogen, nitrogen, and fluorine atoms. Because of the small magnitude of the exchange coupling constants, all energy calculations must be performed, including the SCF = Tight option of Gaussian code, to ensure sufficiently well converged values for the state energies.

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- [1] O. Kahn, *Molecular Magnetism*, VCH, New York, **1993**.
- [2] *Magnetism: Molecules to Materials* (Eds.: J. S. Miller, M. Drillon), Vols. 1–5, Wiley-VCH, Weinheim, **2001–2005**.
- [3] E. Ruiz, P. Alemany, S. Alvarez, J. Cano, *J. Am. Chem. Soc.* **1997**, *119*, 1297.
- [4] E. Ruiz, S. Alvarez, A. Rodríguez-Forteza, P. Alemany, Y. Pouillon, C. Massobrio, in *Magnetism: Molecules to Materials*, Vol. 2 (Eds.: J. S. Miller, M. Drillon), Wiley-VCH, Weinheim, **2001**, p. 227.
- [5] R. Caballol, O. Castell, F. Illas, P. R. Moreira, J. P. Malrieu, *J. Phys. Chem. A* **1997**, *101*, 7860.
- [6] E. Ruiz, *Struct. Bonding (Berlin)* **2004**, *113*, 71.
- [7] E. Ruiz, J. Cano, S. Alvarez, *Chem. Eur. J.* **2005**, *11*, 4767.
- [8] E. Ruiz, G. Rajaraman, S. Alvarez, B. Gillon, J. Stride, R. Clerac, J. Larionova, S. Decurtins, *Angew. Chem.* **2005**, *117*, 2771; *Angew. Chem. Int. Ed.* **2005**, *44*, 2711.
- [9] D. B. Amabilino, J. Veciana, in *Magnetism: Molecules to Materials*, Vol. 2 (Eds.: J. S. Miller, M. Drillon), Wiley-VCH, Weinheim, **2001**, p. 1.
- [10] H. Iwamura, K. Inoue, in *Magnetism: Molecules to Materials*, Vol. 2 (Eds.: J. S. Miller, M. Drillon), Wiley-VCH, Weinheim, **2001**, p. 61.
- [11] R.-J. Bushby, in *Magnetism: Molecules to Materials*, Vol. 2 (Eds.: J. S. Miller, M. Drillon), Wiley-VCH, Weinheim, **2001**, p. 149.
- [12] C. Faulmann, P. Cassoux, *Prog. Inorg. Chem.* **2004**, *52*, 399.
- [13] N. Avarvari, M. Fourmigue, *Chem. Commun.* **2004**, 1300.
- [14] T. Devic, J. N. Bertran, B. Domercq, E. Canadell, N. Avarvari, P. Auban-Senzier, M. Fourmigue, *New J. Chem.* **2001**, *25*, 1418.
- [15] K. Heuze, M. Fourmigue, P. Batail, E. Canadell, P. Auban-Senzier, *Chem. Eur. J.* **1999**, *5*, 2971.
- [16] J. L. Musfeldt, in *Magnetism: Molecules to Materials*, Vol. 1 (Eds.: J. S. Miller, M. Drillon), Wiley-VCH, Weinheim, **2001**, p. 95.
- [17] M. C. Cross, *Phys. Rev. B* **1979**, *20*, 4606.
- [18] M. C. Cross, D. S. Fisher, *Phys. Rev. B* **1979**, *19*, 402.
- [19] C. Rovira, *Chem. Eur. J.* **2000**, *6*, 1723.
- [20] C. Rovira, *Struct. Bonding (Berlin)* **2001**, *100*, 163.
- [21] H. Imai, T. Otsuka, T. Naito, K. Awaga, T. Inabe, *J. Am. Chem. Soc.* **1999**, *121*, 8098.
- [22] B. Domercq, C. Coulon, M. Fourmigue, *Inorg. Chem.* **2001**, *40*, 371.
- [23] M. Fourmigue, B. Domercq, I. V. Jourdain, P. Molinie, F. Guyon, J. Amaudrut, *Chem. Eur. J.* **1998**, *4*, 1714.
- [24] P. Batail, C. Livage, S. S. P. Parkin, C. Coulon, J. D. Martin, E. Canadell, *Angew. Chem.* **1991**, *103*, 1508; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 1498.
- [25] M. Fourmigue, *Acc. Chem. Res.* **2004**, *37*, 179.
- [26] R. Clerac, M. Fourmigue, C. Coulon, *J. Solid State Chem.* **2001**, *159*, 413.
- [27] R. Clerac, M. Fourmigue, J. Gaultier, Y. Barrans, P. A. Albouy, C. Coulon, *Eur. Phys. J. B* **1999**, *9*, 431.
- [28] R. Clerac, M. Fourmigue, J. Gaultier, Y. Barrans, P. A. Albouy, C. Coulon, *Eur. Phys. J. B* **1999**, *9*, 445.
- [29] B. Domercq, C. Coulon, P. Feneyrou, V. Dentan, P. Robin, M. Fourmigue, *Adv. Funct. Mater.* **2002**, *12*, 359.
- [30] M. Fourmigue, C. Coulon, *Adv. Mater.* **1994**, *6*, 948.
- [31] C. Faulmann, F. Delpech, I. Malfant, P. Cassoux, *J. Chem. Soc. Dalton Trans.* **1996**, 2261.
- [32] M. Fourmigue, N. Avarvari, *Dalton Trans.* **2005**, 1365.
- [33] M. Nomura, T. Cauchy, M. Geoffroy, P. Adkine, M. Fourmigue, *Inorg. Chem.* **2006**, *45*, 8194.
- [34] M. Nomura, M. Geoffroy, P. Adkine, M. Fourmigué, *Eur. J. Inorg. Chem.* **2006**, 5012.
- [35] *Prog. Inorg. Chem.* (Ed.: E. I. Stiefel), **2004**, Vol. 52.
- [36] N. Robertson, L. Cronin, *Coord. Chem. Rev.* **2002**, *227*, 93.
- [37] T. M. Barclay, A. W. Cordes, N. A. George, R. C. Haddon, M. E. Itkis, M. S. Mashuta, R. T. Oakley, G. W. Patenaude, R. W. Reed, J. F. Richardson, H. Zhang, *J. Am. Chem. Soc.* **1998**, *120*, 352.
- [38] J. L. Brusso, O. P. Clements, R. C. Haddon, M. E. Itkis, A. A. Leitch, R. T. Oakley, R. W. Reed, J. F. Richardson, *J. Am. Chem. Soc.* **2004**, *126*, 14692.
- [39] J. L. Brusso, O. P. Clements, R. C. Haddon, M. E. Itkis, A. A. Leitch, R. T. Oakley, R. W. Reed, J. F. Richardson, *J. Am. Chem. Soc.* **2004**, *126*, 8256.
- [40] A. Alberola, R. J. Collis, S. M. Humphrey, R. J. Less, J. M. Rawson, *Inorg. Chem.* **2006**, *45*, 1903.
- [41] A. J. Banister, N. Bricklebank, I. Lavender, J. M. Rawson, C. I. Gregory, B. K. Tanner, W. Clegg, M. R. J. Elsegood, F. Palacio, *Angew. Chem.* **1996**, *108*, 2648; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2533.
- [42] M. Nomura, R. Okuyama, C. Fujita-Takayama, M. Kajitani, *Organometallics* **2005**, *24*, 5110.
- [43] M. Fourmigué, J. N. Bertran, *Chem. Commun.* **2000**, 2111.
- [44] R. B. King, M. B. Bisnette, *Inorg. Chem.* **1967**, *6*, 469.
- [45] C. G. Krespan, B. C. McKusick, *J. Am. Chem. Soc.* **1961**, *83*, 3438.
- [46] O. Jeannin, M. Fourmigue, *Chem. Eur. J.* **2006**, *12*, 2994.
- [47] C. Maletzko, W. Sundermeyer, H. Pritzkow, H. Irngartner, U. Huberpatz, *Chem. Ber.* **1991**, *124*, 2025.
- [48] H. Guth, G. Heger, U. Druck, *Z. Kristallogr.* **1982**, *159*, 185.
- [49] G. R. Desijaru, T. Steiner, *The Weak Hydrogen Bond in Structural Chemistry and Biology*, Vol. 9, Oxford University Press, Oxford, **1999**.
- [50] B. Bleaney, K. D. Bowers, *Proc. Phys. Soc. London Sect. A* **1952**, *65*, 667.
- [51] J. C. Bonner, M. E. Fisher, *Phys. Rev. A* **1964**, *135*, 640.
- [52] C. Desplanches, E. Ruiz, A. Rodríguez-Forteza, S. Alvarez, *J. Am. Chem. Soc.* **2002**, *124*, 5197.
- [53] J. S. Miller, J. C. Calabrese, H. Rommelmann, S. R. Chittipeddi, J. H. Zhang, W. M. Reiff, A. J. Epstein, *J. Am. Chem. Soc.* **1987**, *109*, 769.
- [54] E. Ruiz, J. Cano, S. Alvarez, P. Alemany, *J. Comput. Chem.* **1999**, *20*, 1391.
- [55] W. Koch, M. C. Holthausen, *A Chemist's Guide to Density Functional Theory*, Wiley-VCH, Weinheim, **2000**.
- [56] E. Ruiz, S. Alvarez, J. Cano, V. Polo, *J. Chem. Phys.* **2005**, *123*.
- [57] A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648.
- [58] Gaussian 03 (Revision C.1), M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, H. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, Gaussian, Inc., Pittsburgh, PA, **2003**.
- [59] Jaguar 6.0, Schrödinger, Inc., Portland, **2005**.
- [60] F. Weigend, F. Furche, R. Ahlrichs, *J. Chem. Phys.* **2003**, *119*, 12753.

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