

The contrasted structural and magnetic behaviour of two single-component paramagnetic dithiolene complexes

Mitsushiro Nomura and Marc Fourmigué*

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The neutral organometallic/dithiolene radical complexes [CpNi(oxddt)] and [CpNi(bddt)] were prepared, respectively, from the reactions of [Ni(oxddt)₂] with [Cp₂Ni] and (NBu₄)[Ni(bddt)₂] with [CpNi(cod)](BF₄) (oxddt = *o*-xylenediyldithioethylene-1,2-dithiolato, bddt = 1,4-butanediyl dithioethylene-1,2-dithiolato). Both complexes exhibit reversible oxidation and reduction waves to the cation and anion forms, respectively. A NIR absorption is observed around $\lambda_{\text{max}} = 825$ nm for [CpNi(oxddt)] and 774 nm for [CpNi(bddt)] in dichloromethane solution. The X-ray crystal structures of the two complexes show two-legged piano-stool geometries around the central nickel atom (formally Ni^{III}) and strong distortions from planarity of the eight-membered ring moieties. In the solid state, the stronger rigidity of [CpNi(oxddt)] allows for a face-to-face π - π stacking of the radicals into dyads, confirmed by a singlet–triplet magnetic behaviour while the more flexible [CpNi(bddt)] radical complexes only interact through a lateral antiferromagnetic interaction giving rise to Heisenberg-type uniform spin chains.

Introduction

Metal dithiolene complexes have been extensively investigated due to their combination of functional properties, specific geometries, and intermolecular interactions that confer them an enormous interest in the field of magnetism,¹ conductivities,² and optical properties.³ The metal dithiolene complexes involve not only homoleptic types such as bis(dithiolene) [M(dithiolene)₂]^{*n*−} (M = Ni, Pd, Pt),⁴ tris(dithiolene) [M(dithiolene)₃]^{*n*−} (M = V, Cr, Mo, W, Re),⁵ (Nd, Ce,⁶ U)⁷ and tetrakis(dithiolene) [M(dithiolene)₄]^{*n*−} (M = Ce, U),^{7,8} which are composed only of dithiolene ligands, but also heteroleptic ones such as [M(dithiolene)L₂] (M = Ni, Pd, Pt)⁹ and organometallic dithiolene complexes. The latter organometallic dithiolene complexes include [(Cp)_{*n*}M(dithiolene)_{*n*}] (Cp = η^5 -cyclopentadienyl),¹⁰ [(η^6 -C₆R₆)M(dithiolene)] (M = Ru)¹¹ and [(η^4 -C₄R₄)M(dithiolene)] (M = Ni, Pd).¹² They have electron-deficient metal centres, which are stabilized by a π -electron donation of the dithiolene ligands¹³ and by the π -coordinated organometallic ligand.

Different series of paramagnetic complexes such as the cationic d¹ [Cp₂Mo(dithiolene)]⁺ have shown a wide variety of magnetic behaviours, from uniform spin chains to spin ladders or antiferromagnetic ground states, depending strongly on the size, shape and charge of the counter ion.¹⁴ On the other hand, [CpNi^{III}(dithiolene)][•] complexes are paramagnetic (*S* = 1/2) in their neutral states.¹⁵ Namely, these species belong to a larger group of single-component magnetic dithiolene complexes such as [Au^{IV}(dithiolene)₂],¹⁶ [CpMo^V(dithiolene)₂]¹⁷ or [CpCo^{IV}(Br)(dithiolene)],¹⁸ where strong

intermolecular interactions can develop in the solid state in the absence of any counter ions. For example, some single-component radical [CpNi^{III}(dithiolene)] complexes have shown unexpectedly strong antiferromagnetic interactions due not only to dithiolene/dithiolene contacts as anticipated but also to Cp[•] · Cp face-to-face overlap.^{15c}

We have recently reported the synthesis and properties of such CpNi(dithiolene) complexes functionalized with, (i) a simple R substituent as in [CpNi(S₂C₂R₂)] with R = CN, COOMe, Ph, Me,^{15b} (ii) sulfur-rich outer rings as in [CpNi(dmit)] (dmit = 1,3-dithiol-2-thione-4,5-dithiolato)^{15a} and [CpNi(dddt)] (dddt = 5,6-dihydro-1,4-dithiin-2,3-dithiolato) groups,^{15c} (iii) a rigid six-membered ring in [CpNi(bdt)] (bdt = 1,2-benzenedithiolato),^{15c,e} and (iv) a flexible seven-membered ring as in [CpNi(pddt)] (pddt = 1,3-propanediyl dithioethylene-1,2-dithiolato) and its analogues (Chart 1).^{15d}

The structural and magnetic behaviour of these complexes was shown to be highly dependent on the nature and steric constraints of the substituents on the dithiolene ligand, offering a wide variety of possible magnetic interactions (dyadic associations with singlet–triplet behaviour, alternated or

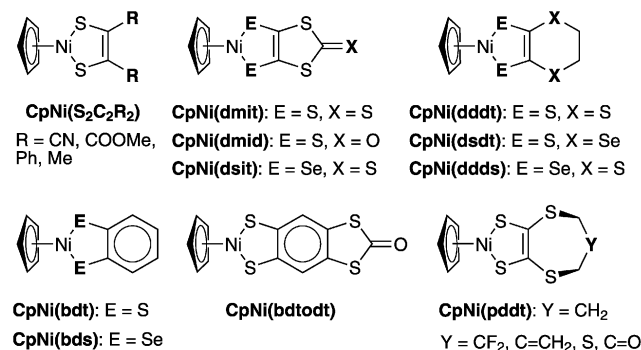


Chart 1

Sciences Chimiques de Rennes, UMR 6226 CNRS-Université de Rennes 1, Equipe MaCSE, Campus de Beaulieu, 35042 Rennes cedex, (France). E-mail: marc.fourmigue@univ-rennes1.fr; Fax: (+33) 2 23 23 67 32

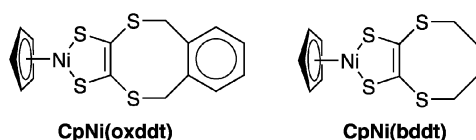


Chart 2

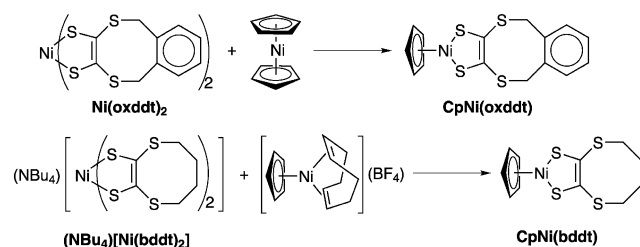
uniform chains through lateral S...S contacts, antiferromagnetic three-dimensional ground state), even for closely related molecular structures. In order to get a further insight in this extensive family, we have investigated two further neutral radical complexes where the metallacycle is now fused with a larger and flexible eight-membered ring, namely the [CpNi(oxddt)] (oxddt = *o*-xylenediyldithioethylene-1,2-dithiolato) and [CpNi(bddt)] (bddt = 1,4-butanediyl-dithioethylene-1,2-dithiolato) complexes shown in Chart 2.

While both complexes are expected to exhibit closely related electronic structures and spin delocalisation, their structural and accordingly magnetic behaviour in the solid state might strongly depend on the shape adopted by the eight-membered outer ring. Indeed, the anticipated stronger rigidity of the *o*-xylylene derivative will contrast with the more flexible character of the 1,4-butylene one. We report here the preparation, electronic properties, X-ray crystal structures, and magnetic properties of the two complexes, showing that they are indeed characterized by completely different structural and magnetic properties, intimately related to the different ways such radical molecules manage to increase chemical bonding in the solid state, either through *localized* 2e bonds or through *delocalized* one-dimensional antiferromagnetic spin chains.

Results and discussion

Syntheses and molecular structures of [CpNi(oxddt)] and [CpNi(bddt)]

The formally Ni^{III} species can be obtained either from the reaction of the two charged Ni^{III} species, [Ni(dithiolene)₂][−] and [Cp₂Ni]⁺, or from the reaction of the Ni^{II} [Cp₂Ni] with the formally Ni^{IV} [Ni(dithiolene)₂]⁰.¹⁵ Accordingly, the reaction of the neutral square-planar dithiolene complex [Ni(oxddt)₂] with [Cp₂Ni] in toluene (80 °C) gave [CpNi(oxddt)] in 44% yield (Scheme 1). However, the corresponding [Ni(bddt)₂] reacted with [Cp₂Ni] to form [CpNi(bddt)] only in a low yield. On the other hand, the reaction of (NBu₄)[Ni(bddt)₂] with [CpNi(cod)](BF₄) in refluxing methanol afforded [CpNi(bddt)] in an improved 30% yield



Scheme 1

(Scheme 1). This method using [CpNi(cod)](BF₄) as a Ni^{II} precursor has been recently developed during the optimization of synthesis of [CpNi(dddt)].^{15c} Conveniently, the neutral [CpNi(dithiolene)] complexes are easy to separate from these ionic components by column chromatography on silica gel. Both products are air-stable at room temperature, and are more soluble in typical organic solvents (dichloromethane, toluene, acetone and THF) than the other [CpNi(dithiolene)] complexes shown in Chart 1.

The ORTEP drawings of [CpNi(oxddt)] and [CpNi(bddt)] are shown in Fig. 1. [CpNi(oxddt)] and [CpNi(bddt)] crystallize in the triclinic (*P* $\bar{1}$ space group) and monoclinic crystal systems (*P*2₁/*n*), respectively, with one crystallographically independent molecule in the unit cell for both compounds.

The complexes have two-legged piano-stool geometries with molecular geometries similar to the 16-electron [CpM(dithiolene)] (M = Co, Rh, Ir) and [η^6 -C₆R₆]Ru(dithiolene)] complexes. Selected bond lengths (Å), bond angles and dihedral angles (°) are summarized in Tables 1 and 2, respectively. The Ni–S bond lengths in [CpNi(oxddt)] and [CpNi(bddt)] are *ca.* 2.13 Å and these lengths are slightly longer than in other [CpNi(dithiolene)] complexes (*ca.* 2.12 Å) except for [CpNi(dmit)] (Ni–S 2.13 Å). In general, the Ni–S lengths in [CpNi(dithiolene)] are longer than the Co–S lengths in [CpCo(dithiolene)] complexes (2.10–2.11 Å).^{10,19} This result suggests different π -electron donating effect from sulfur to metal¹³ in the Ni and Co dithiolene rings, namely, the difference between 17-electron (Ni^{III}) and 16-electron (Co^{III}) dithiolene complexes. Furthermore, in the comparison of [CpNi(bddt)] with the corresponding square-planar Ni dithiolene complex (NEt₄)[Ni(bddt)₂] (Table 1), the Ni–S length in [CpNi(bddt)] is slightly shorter than that of (NEt₄)[Ni(bddt)₂] (Ni–S 2.15 Å).²⁰ Similar tendencies have been observed between [CpNi(pddt)] and [Ni(pddt)₂] monoanion series.^{15d,21}

In fact, the dihedral angles (θ_1) between the Cp and NiS₂ mean planes are almost 90° (Fig. 1 and Table 2). The five-membered nickeladithiolene plane (NiS₂C₂) is quite planar. This plane is folded along the S...S hinge making the θ_2 angle (Fig. 1 and Table 2). The θ_2 values in [CpNi(oxddt)] and [CpNi(bddt)] are 8.78 and 4.54°, respectively. The θ_3 angle in Fig. 1 is the large folding of eight-membered ring moiety along the S...S hinge. The θ_3 values of [CpNi(oxddt)] and [CpNi(bddt)] are 64.42 and 77.69°. These values are much larger than the θ_3 values of the [CpNi(dithiolene)] complexes with a seven-membered ring (θ_3 = 61–67°).^{15d} Probably, the eight-membered ring moiety is significantly distorted by the flexibility of the terminal butylene group.

Electronic properties

The cyclic voltammograms (CV) of [CpNi(oxddt)] and [CpNi(bddt)] showed well-defined reversible reduction waves at −1.07 and −1.04 V (*vs.* Fc/Fc⁺), and reversible oxidation waves at 0.16 and 0.14 V, respectively (Table 3).

The reduction potentials are essentially similar to those of [CpNi(dddt)] (−1.06 V) and [CpNi(pddt)] (−1.08 V). On the other hand, the oxidation potentials are slightly more anodic than those of the corresponding six-membered [CpNi(dddt)] (−0.02 V) and seven-membered [CpNi(pddt)] (+0.07 V)

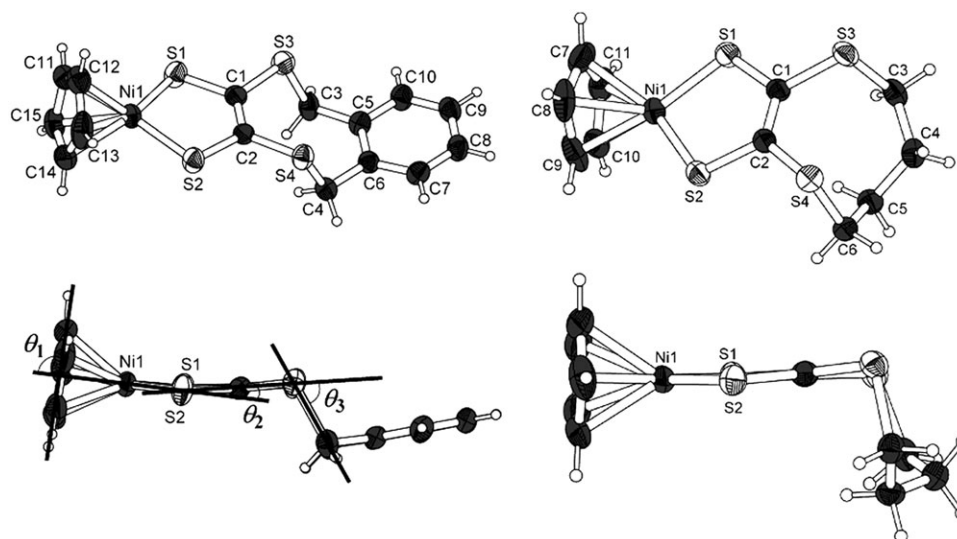


Fig. 1 The ORTEP drawings of [CpNi(oxddt)] and [CpNi(bddt)] with thermal ellipsoids drawn at 50% probability level: (top left) [CpNi(oxddt)] showing all the atoms, (bottom left) a side view showing the definition of the three folding angles θ_{1-3} reported in Table 2; θ_1 is the dihedral angle ($^\circ$) between the Cp and NiS₂ mean planes, θ_2 represents the small folding of the metallacycle along the S...S hinge, and θ_3 is the large folding of the seven-membered ring along the S...S hinge, (top right and bottom right) [CpNi(bddt)].

Table 1 Selected bond lengths (Å) in [CpNi(oxddt)], [CpNi(bddt)] and reference complexes

	Ni1–S1	Ni1–S2	S1–C1	S2–C2	C1–C2	Ref.
[CpNi(oxddt)]	2.133(3)	2.121(3)	1.734(9)	1.720(8)	1.353(13)	This work
[CpNi(bddt)]	2.1320(18)	2.1255(16)	1.738(5)	1.739(6)	1.337(7)	This work
(NEt ₄)[Ni(bddt) ₂]	2.148(4)	2.156(3)	1.690(13)	1.748(13)	1.368(18)	20
[CpNi(pddt)]	2.1242(10)	2.1242(10)	1.725(3)	1.726(3)	1.358(5)	15d
[CpNi(dddt)]	2.125(2)	2.127(2)	1.711(10)	1.744(9)	1.336(13)	15c
[CpNi(bdt)]	2.1205(13)	2.1280(13)	1.731(5)	1.740(4)	1.410(6)	15c
[CpNi(dmit)]	2.138(2)	2.133(2)	1.706(8)	1.716(7)	1.36(1)	15a
[CpNi(mnt)]	2.1255(8)	2.1282(8)	1.715(3)	1.725(3)	1.354(4)	15b

Table 2 Selected bond angles ($^\circ$) in [CpNi(oxddt)], [CpNi(bddt)] and reference complexes^a

	S1–Ni1–S2	Ni–S1–C1	Ni1–S2–C2	θ_1	θ_2	θ_3	Ref.
[CpNi(oxddt)]	91.66(10)	103.9(3)	105.0(3)	87.37	8.78	64.42	This work
[CpNi(bddt)]	92.34(6)	103.7(2)	103.90(19)	88.87	4.54	77.69	This work
(NEt ₄)[Ni(bddt) ₂]	91.5(1)	104.9(5)	103.9(4)	—	—	—	20
[CpNi(pddt)]	92.42(4)	103.97(11)	103.85(11)	89.3	7.7	61.32	15d
[CpNi(dddt)]	92.42(9)	103.4(3)	103.7(3)	86.9	1.0, 4.3	—	15d
[CpNi(bdt)]	93.93(5)	103.71(15)	103.61(15)	84.9	2.7, 5.0	—	15c
[CpNi(dmit)]	94.97(8)	100.8(3)	100.9(3)	86.5	4.0	—	15c
[CpNi(mnt)]	94.61(3)	101.7(1)	101.7(1)	89.9	1.4	—	15a

^a The dihedral angles θ_1 , θ_2 and θ_3 are defined in Fig. 1.

complexes. Generally, we have observed that the nature of the dithiolene ligand strongly affects their oxidation potentials. For example, in the [CpNi(pddt)] complexes and analogs (Chart 1), the terminal Y groups (Y = CH₂, CF₂, C=CH₂, S, C=O) in the seven-membered ring strongly shift their oxidation potentials to anodic potentials in the following order: CF₂ > C=O > S > C=CH₂ > CH₂.^{15d} Furthermore, in the comparison of [CpNi(dddt)] and [CpNi(bdt)], there is a large difference of oxidation potential (−0.02 and +0.30 V) despite their similar reduction potentials (Table 3). It therefore

appears that the flexibility introduced by the eight-membered rings in [CpNi(oxddt)] and [CpNi(bddt)] probably controls the way the two sulfur atoms of these rings contribute to the frontier orbitals, by modifying the relative orientation of the sulfur lone pairs relative to the NiS₂C₂ metallacycle mean plane.

The UV-Vis-NIR spectra of [CpNi(oxddt)] and [CpNi(bddt)] are displayed in Fig. 2 and the spectral data (λ_{max}) are summarized in Table 4. [CpNi(oxddt)] and [CpNi(bddt)] exhibit absorption maxima at 825 and 774 nm

Table 3 Redox potentials of [CpNi(oxddt)], [CpNi(bddt)] and reference complexes

	$E_{1/2}$ (red)/V (vs. Fc/Fc ⁺)	ΔE /mV	ΔE_p /mV	$E_{1/2}$ (ox)/V (vs. Fc/Fc ⁺)	ΔE /mV	ΔE_p /mV	Ref.
[CpNi(oxddt)]	−1.07	68	94	+0.16	68	94	This work
[CpNi(bddt)]	−1.04	62	65	+0.14	62	60	This work
[CpNi(S ₂ C ₂ S ₂ (CH ₂) ₃)]	−1.08	70	100	+0.07	68	92	15d
[CpNi(S ₂ C ₂ S ₂ (CH ₂) ₂ (S))]	−1.02	70	98	+0.19	72	98	15d
[CpNi(S ₂ C ₂ S ₂ (CH ₂) ₂ (CF ₂))]	−0.98	72	102	+0.25	72	98	15d
[CpNi(S ₂ C ₂ S ₂ (CH ₂) ₂ (C=CH ₂))]	−1.05	72	100	+0.12	72	100	15d
[CpNi(S ₂ C ₂ S ₂ (CH ₂) ₂ (C=O))]	−0.98	68	104	+0.22	68	98	15d
[CpNi(dddtt)]	−1.06	72	106	−0.02	74	106	15c
[CpNi(bdt)]	−1.00	68	92	+0.30	72	88	15c

$E_{1/2} = (E_p + E_{p/2})/2$, $\Delta E = |E_p - E_{p/2}|$, $\Delta E_p = |E_{pa} - E_{pc}|$.

in dichloromethane, respectively. The absorption maximum of [CpNi(oxddt)] is as for [CpNi(dithiolene)] complexes with a seven-membered ring (798–848 nm). On the other hand, [CpNi(bddt)] exhibits a blue shift compared with them. Interestingly, the absorption maximum of the butylene derivative [CpNi(bddt)] strongly differs from the propylene [CpNi(pddt)] (848 nm) or ethylene [CpNi(dddtt)] (1012 nm in Table 4) derivatives (Chart 3).

This result clearly suggests that modifications of the outer substituents of the dithiolene core can modify the electronic absorption energy, even when the modification is limited to the substitution: ethylene vs. propylene vs. butylene. As already mentioned from the electrochemical results, this absorption energy blue shift is most probably related to the planarity and distortions of the outer substituents of the dithiolene core (see θ_3 in Table 2).

Solid-state structural and magnetic properties

A projection view of the unit cell of the more flexible [CpNi(bddt)] complex is shown in Fig. 3 together with the shortest intermolecular S...S contacts identified in the structure. There are no other contacts along the third *a* direction. This short S...S contact at 3.893 Å is established between a sulfur atom of the metallacycle and a sulfur atom of the eight-membered ring. While a sizeable part of the spin distribution can be anticipated on the metallacycle sulfur atom, a weaker

one probably characterizes the other one. As a consequence, a weak magnetic interaction is expected, which would develop, for symmetry reasons, into a regular one-dimensional spin chain.

The temperature dependence of the magnetic susceptibility of [CpNi(bddt)], determined from the SQUID measurement on a polycrystalline sample at 5000 G, indeed confirms this structural analysis (Fig. 4). The susceptibility exhibits a rounded maximum around 50 K, demonstrating the presence of antiferromagnetic interactions, with only a weak decrease below 50 K, excluding the possibility of a singlet ground state. A fit of the experimental data with the Bonner–Fisher model,²² taking into account a small contribution of magnetic defaults, observable at low temperatures, was used (eqn (1)):

$$\chi_{\text{mol}} = \chi_0 + x\chi_{\text{Curie}} + (1 - x)\chi_{\text{BF}} \quad (1)$$

where χ_0 is a temperature independent contribution, x the fraction of paramagnetic defaults and χ_{BF} the Bonner–Fischer susceptibility, expressed by a numerical expression²³ depending on J for the corresponding Hamiltonian (eqn (2)):

$$H = -J \sum_{i=1}^{n-1} S_i S_{i+1}. \quad (2)$$

Considering an averaged g value¹⁵ of 2.05 for both the Curie tail and magnetic chain contributions, one obtains the following values from the fit: $\chi_0 = 3.00 \times 10^{-4} \text{ cm}^3 \text{ mol}^{-1}$, $x = 1.1\%$, $J/k = -71.1(4) \text{ K}$, that is $J = -49 \text{ cm}^{-1}$.

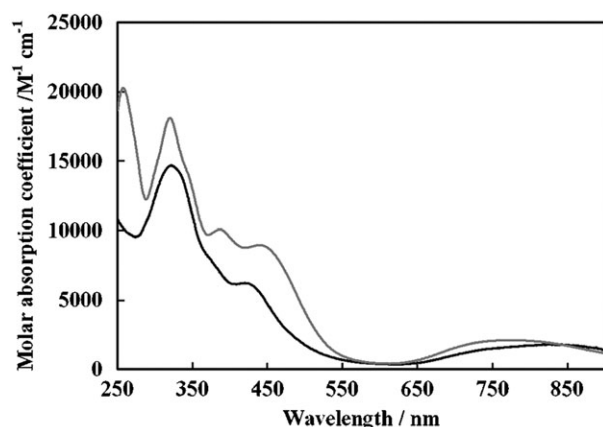


Fig. 2 UV-Vis-NIR spectra of [CpNi(oxddt)] (black line) and [CpNi(bddt)] (gray line) in dichloromethane solution.

Table 4 UV-Vis-NIR data of all [CpNi(dithiolene)] complexes

	$\lambda_{\text{max}}/\text{nm}$	$\epsilon/\text{M}^{-1} \text{ cm}^{-1}$	Ref.
[CpNi(dddtt)]	1012	4700	15c
[CpNi(dmit)]	967	6000	15c
[CpNi(S ₂ C ₂ Ph ₂)]	846	2900	15b
[CpNi(S ₂ C ₂ Me ₂)]	835	2600	15b
[CpNi(S ₂ C ₂ S ₂ (CH ₂) ₃)]	848	2100	15d
[CpNi(S ₂ C ₂ S ₂ (CH ₂) ₂ (C=CH ₂))]	840	2400	15d
[CpNi(oxddt)]	825	1900	This work
[CpNi(S ₂ C ₂ S ₂ (CH ₂) ₂ (S))]	823	1800	15d
[CpNi(S ₂ C ₂ S ₂ (CH ₂) ₂ (C=O))]	806	1700	15d
[CpNi(S ₂ C ₂ S ₂ (CH ₂) ₂ (CF ₂))]	798	2000	15d
[CpNi(bddt)]	774	2100	This work
[CpNi(bdtodt)]	741	6000	15e
[CpNi(bdt)]	722	2600	15c
[CpNi(mnt)]	698	2000	15b
[CpNi(S ₂ C ₂ (CO ₂ Me) ₂)]	695	1500	15b

All UV-Vis-NIR spectra were measured in dichloromethane solution.

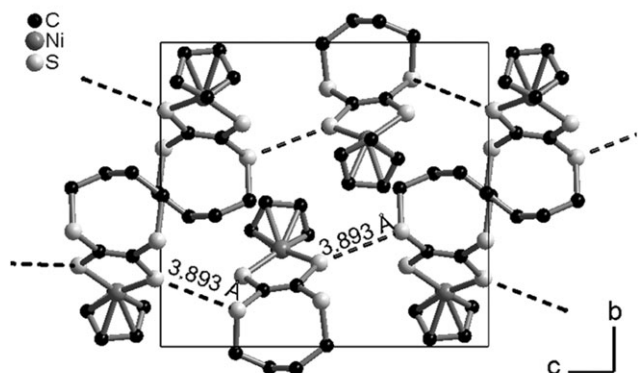
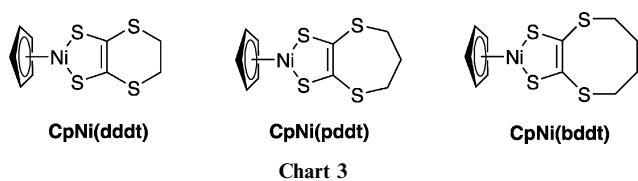


Fig. 3 Projection view along *a* of the unit cell of [CpNi(bddtt)] showing the uniform chain structure running along *c*.

As shown below in Fig. 5 and 6, the solid-state structure adopted with the more rigid *o*-xylylene derivative [CpNi(oxddt)] is very different. The molecules organize into inversion-centred dyads, weakly connected along the *a* direction (Fig. 5) while a stronger overlap can be anticipated from the perfect, almost eclipsed, face-to-face overlap of the planar C₂S₄ moieties within the dyads (Fig. 6). This structural “hand-made” analysis is confirmed by the temperature dependence of the magnetic susceptibility. As shown in Fig. 4, it exhibits an acute maximum around 28 K, together with a singlet ground state at the lowest temperatures and an activated susceptibility between these two regimes, a behaviour characteristic of the presence of a spin gap. Accordingly, a fit of the experimental

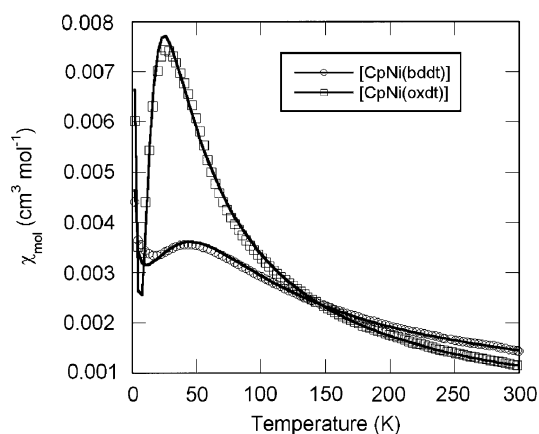


Fig. 4 Temperature dependence of the magnetic susceptibility of [CpNi(bddtt)] (○) and [CpNi(oxddt)] (□). The solid lines are fits to the uniform Heisenberg spin chain model for [CpNi(bddtt)] and to the singlet–triplet model for [CpNi(oxddt)] (see text).

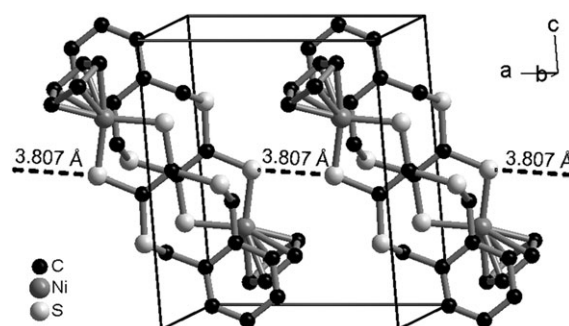


Fig. 5 A view of the short intermolecular S...S interactions running along the *a* direction in [CpNi(oxddt)].

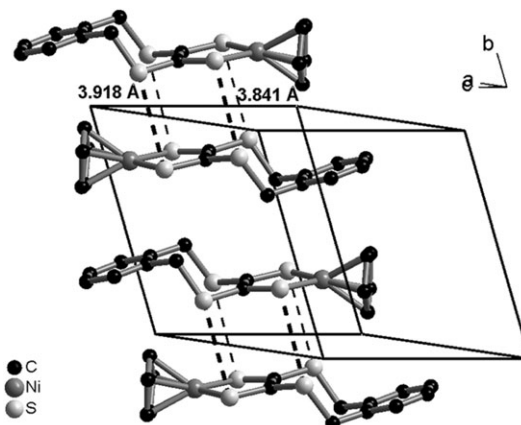


Fig. 6 A view of the stacking of [CpNi(oxddt)] radical complexes along the *b* direction, showing the inversion-centred dyadic association.

data, expressed by eqn (3):

$$\chi_{\text{mol}} = \chi_0 + x\chi_{\text{Curie}} + (1-x) \frac{Ng^2\beta^2}{kT[3 + \exp(-J/kT)]}, \quad (3)$$

was performed with a *g* value of 2.05 for both contributions, affording $\chi_0 = -1.54 \times 10^{-4} \text{ cm}^3 \text{ mol}^{-1}$, $x = 3.4\%$ and $J/k = -41.7(4) \text{ K}$, that is $J = -29 \text{ cm}^{-1}$.²⁴ The effectiveness of the singlet–triplet model to fit the magnetic susceptibility of [CpNi(oxddt)] also demonstrates that the localized magnetic interaction within the dyadic entities shown in Fig. 6 dominates the magnetic behaviour of the whole system. Considering the extra S...S interaction running along *a* and shown in Fig. 5, leads us to describe this material as a strongly alternated magnetic chain, with typically a similar temperature dependence of the magnetic susceptibility.

Conclusions

The two neutral radical organometallic complexes described here provide a striking example of the extreme sensitivity of the electronic and magnetic properties of such organometallic complexes to minor modifications of the substituents on the dithiolene core. Comparison of the two complexes with a similar fused eight-membered ring demonstrates how its rigidification in [CpNi(oxddt)] brought by the outer benzene ring

completely modifies its packing in the solid state while the lower symmetry adopted by the butylene derivative [CpNi(bddt)] hinders the face-to-face dyadic association and thus favours an extended one-dimensional magnetic chain structure through lateral S...S interactions. Another impressive variability encountered in these series is found in their spectroscopic properties and specifically their NIR absorption energy. Comparison of the ethylene, propylene and butylene derivatives (Chart 3) shows a very large blue shift, from 1012 nm in [CpNi(dddt)] to 848 nm in [CpNi(pddt)] and 774 nm in [CpNi(bddt)]. This evolution correlates also with the increasing $E^{1/2}$ (vs. Fc^+/Fc) oxidation potentials, from -0.02 V in [CpNi(dddt)] to $+0.07$ V in [CpNi(pddt)] and $+0.14$ V in [CpNi(bddt)]. Theoretical TD-DFT calculations will be performed in order to understand the origin of these NIR absorption bands and their evolution within these apparently simple series.

Experimental

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 CaH_2 (for methanol) before use. The square-planar nickel dithiolene complexes $[\text{Ni}(\text{oxddt})_2]^{25}$ and $(\text{NBu}_4)[\text{Ni}(\text{bddt})_2]^{20,26}$ were synthesized by literature methods. $[\text{CpNi}(\text{cod})](\text{BF}_4)$ was prepared by a literature method.²⁷ $[\text{Cp}_2\text{Ni}]$ was obtained from STREM Chemicals and Aldrich Chemicals, respectively. Silica gel (Silica gel 60) was obtained from MERCK, Ltd. TOF-mass spectra were recorded on a Bruker Daltonics MALDI-TOF BIFLEX III mass spectrometer. UV-Vis and NIR spectra were recorded on a Hitachi Model UV-2500PC and a Shimadzu Model UV-1605 spectrophotometer. Elemental analyses were performed by the "Service d'Analyse du CNRS" at Gif/Yvette, France.

Preparation of [CpNi(oxddt)] from neutral starting materials $[\text{Ni}(\text{oxddt})_2]$ and $[\text{Cp}_2\text{Ni}]$

A toluene solution of $[\text{Cp}_2\text{Ni}]$ (53 mg, 0.28 mmol) and $[\text{Ni}(\text{oxddt})_2]$ (160 mg, 0.28 mmol) was reacted under 80°C for 2 h. After the solvent was removed under reduced pressure, the residue was separated by column chromatography (silica gel, dichloromethane–*n*-hexane = 1 : 1 (v/v)). The product was further purified by recrystallization (*n*-hexane–dichloromethane) at room temperature. The CpNi dithiolene complex [CpNi(oxddt)] was obtained as black crystals in 44% yield. TOF-Mass (MALDI, 19 kV) 379 (M^+), 275 ($\text{M}^+ - (\text{CH}_2)_2\text{C}_6\text{H}_4$). UV-Vis (CH_2Cl_2) $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{M}^{-1}\text{cm}^{-1}$) 825 (1900), 420 (6100), 321 (14000). Anal. Calc. for $\text{C}_{15}\text{H}_{13}\text{NiS}_4$: C, 47.38; H, 3.45; S, 33.73. Found: C, 47.44; H, 3.56; S, 33.89%.

Preparation of [CpNi(bddt)] from ionic starting materials $(\text{NBu}_4)[\text{Ni}(\text{bddt})_2]$ and $[\text{CpNi}(\text{cod})](\text{BF}_4)$

A methanol solution of $[\text{CpNi}(\text{cod})](\text{BF}_4)$ (64 mg, 0.2 mmol) and $(\text{NBu}_4)[\text{Ni}(\text{bddt})_2]$ (144 mg, 0.2 mmol) was reacted under refluxing for 2 h. After the solvent was removed under reduced

pressure, the residue was separated by column chromatography (silica gel, dichloromethane–*n*-hexane = 2 : 1 (v/v)). The product was further purified by recrystallization (*n*-hexane–dichloromethane) at 0°C . [CpNi(bddt)] was obtained as black crystals in 30% yield. TOF-Mass (MALDI, 19 kV) 331 (M^+), 275 ($\text{M}^+ - (\text{CH}_2)_4$). UV-Vis (CH_2Cl_2) $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{M}^{-1}\text{cm}^{-1}$) 774 (2100), 439 (8800), 387 (9900), 320 (18000), 257 (20000). Anal. Calc. for $\text{C}_{11}\text{H}_{13}\text{NiS}_4$: C, 39.77; H, 3.94. Found: C, 39.68; H, 3.67%.

X-Ray diffraction studies

Single crystals of the [CpNi(oxddt)] and [CpNi(bddt)] complexes were obtained by recrystallization from dichloromethane solutions and then vapor diffusion of *n*-hexane into those solutions at 0°C . Crystals were mounted on the top of a thin glass fiber. Data were collected on a Stoe Imaging Plate Diffraction System (IPDS) with graphite-monochromated Mo-K α radiation ($\lambda = 0.71073$ Å) at room temperature. Structures were solved by direct methods (SHELXS-97) and refined (SHELXL-97)²⁸ by full-matrix least-squares methods, as implemented in the WinGX software package.²⁹ Absorption corrections were applied. Hydrogen atoms were introduced at calculated positions (riding model), included in structure factor calculations, and these were not refined. Crystallographic data for the complexes are summarized in Table 5.

CCDC reference numbers CCDC 630860 for [CpNi(bddt)] and 630861 for [CpNi(oxddt)].

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b700278e

CV measurements

All electrochemical measurements were performed under an argon atmosphere. Solvents for electrochemical measurements

Table 5 Crystallographic data

Compound	[CpNi(oxddt)]	[CpNi(bddt)]
Formula	$\text{C}_{15}\text{H}_{13}\text{NiS}_4$	$\text{C}_{11}\text{H}_{13}\text{NiS}_4$
M_r	380.20	332.16
Crystal color	Black	Black
Crystal size/mm	$0.27 \times 0.21 \times 0.03$	$0.18 \times 0.09 \times 0.09$
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/n$
$a/\text{\AA}$	8.7690(10)	8.5803(12)
$b/\text{\AA}$	9.3180(12)	11.9991(15)
$c/\text{\AA}$	10.3604(15)	12.9458(18)
$\alpha/^\circ$	87.844(16)	
$\beta/^\circ$	83.577(15)	92.406(17)
$\gamma/^\circ$	62.422(13)	
$V/\text{\AA}^3$	745.55(17)	1331.7(3)
T/K	293(2)	293(2)
Z	2	4
$D_c/\text{g cm}^{-3}$	1.694	1.657
μ/mm^{-1}	1.845	2.052
Total refls.	7319	10111
Absorption correction	Multi-scan	Multi-scan
Unique refls. (R_{int})	2714 (0.0954)	2413 (0.1253)
Unique refls. ($I > 2\sigma(I)$)	1577	1330
R_1, wR_2 ($I > 2\sigma(I)$)	0.0752, 0.2006	0.0454, 0.0744
R_1, wR_2 (all data)	0.1208, 0.2299	0.1075, 0.0890
Goodness-of-fit	0.980	0.842
$R_1 = \sum F_o - F_c / \sum F_o $; $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum wF_o^4]^{1/2}$.		

were dried by 4 Å molecular sieves before use. A platinum wire served as a counter electrode, and the SCE (saturated calomel electrode) reference electrode was corrected for junction potentials by being referenced internally to the ferrocene/ferrocenium (Fc/Fc^+) couple. A stationary platinum disk (1.0 mm in diameter) was used as the working electrode. CV measurements were performed with an Autolab PGSTAT 20 potentiostat from Eco Chemie B. V., equipped with General Purpose Electrochemical System GPES software (version 4.5 for Windows). Solution resistance was compensated by positive feedback. 1 mmol dm^{-3} dichloromethane solutions of dithiolene complexes containing 0.1 mol dm^{-3} tetrabutylammonium hexafluorophosphate (NBu_4PF_6) at 25 °C were used for measurements.

Magnetic susceptibility measurements

Magnetic susceptibility measurements were performed on a Quantum Design MPMS-2 SQUID magnetometer operating in the range of 2–300 K at 5000 G with polycrystalline samples of $[\text{CpNi}(\text{oxddt})]$ (4.5 mg) and $[\text{CpNi}(\text{bddt})]$ (6.4 mg). Molar susceptibilities were corrected for Pascal diamagnetism.

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