A series of neutral radical CpNi(dithiolene)• complexes†

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The heteroleptic neutral radical dithiolene complexes CpNi(dmit)[•], CpNi(dsit)[•] and CpNi(dmid)[•] (dmit = 1,3-dithiole-2-thione-4,5-dithiole-2-thione-4,5-diselenolate; dmid = 1,3-dithiole-2-one-4,5-dithiolate) are obtained from the reaction of $(Cp_2Ni)BF_4$ with either $(n-Bu_4N)[Ni(dmit)_2]$ and $(n-Bu_4N)[Ni(dmid)_2]$ or PhSb(dmit) and PhSb(dsit), respectively. The three complexes reduce reversibly to the corresponding Ni(II) anions and oxidize reversibly to the cationic state. As deduced from DFT calculations performed on CpNi(dmit)[•], the SOMO of these complexes is essentially localized on the dithiolene moiety with little metal contribution. CpNi(dsit)[•] is isostructural with CpNi(dmit)[•] and crystallizes in the monoclinic system, space group $P2_1$. In the solid-state structures of both CpNi(dmit)[•] and CpNi(dsit)[•], molecules interact through a three-dimensional set of intermolecular interactions mediated by short $S \cdots S$, $Se \cdots Se$ and $S \cdots Se$ contacts, as confirmed from the temperature and field dependence of the magnetic susceptibility by the observation of an antiferromagnetic ground state below $T_{Neel} = 27$ K in CpNi(dmit)[•], 18 K in CpNi(dsit)[•]. Finally, CpNi(dmid)[•] crystallizes in the orthorhombic system, space group P_{nma} . Molecules organize into uniform chains through the stacking of the dmid moieties in a σ -type face-to-face overlap.

Introduction

Homoleptic dithiolene complexes and among them, the prototypical square-planar nickel bis(dithiolene) complexes, are very well known to exist in several well defined oxidation states,¹ and corresponding radical paramagnetic species have been particularly investigated in the solid state for their conducting or magnetic properties.^{2,3} While strong intermolecular interactions combined with mixed valence allows for the formation of partially filled bands and isolation of conducting or even superconducting materials,4 weaker interactions, most often based on direct exchange between S = 1/2 paramagnetic species lead to antiferromagnetic interactions, giving rise to singlettriplet behaviour in dyadic systems,⁵ but also low dimensional magnetic systems such as spin chains with eventually spin-Peierls transitions⁶ or spin ladders.^{7,8} Ferromagnetic interactions were also observed, essentially in decamethylferrocenium salts9,10 while bulk ferromagnetism was only reported on two cases, that is $[Cp*_2Mn][Ni(dmit)_2]^{11}$ (dmit = 1,3-dithiole-2thione-4,5-dithiolate) and $[NH_4][Ni(mnt)_2] \cdot H_2O$ (mnt = 1,2dicyanoethylene-1,2-dithiolate).12

Antiferromagnetic interactions¹³ were also identified in a family of *heteroleptic* dithiolene complexes¹⁴ which associate both the dithiolate and the cyclopentadienyl ligands as 2 : 1 or 1 : 2 Cp₂M(dithiolene) or CpM(dithiolene)₂ with M = Ti, Zr, Hf, V, Nb, Ta, Mo, W or in 1 : 1 CpM(dithiolene) with M = Co, Rh, Ni species. For example, the 2 : 1 cationic¹⁵ Cp₂M(dithiolene)⁺⁺ and 1 : 2 neutral¹⁶ CpM(dithiolene)₂⁻ d¹ radical complexes with M = Mo, W, adopt a variety of solid-state structures, stabilizing spin chains, spin ladders but also bulk antiferromagnets, an original feature in the magnetism of dithiolene complexes. The occurrence of an antiferromagnetic ground state is the signature of threedimensional interaction networks, favoured in the neutral, but radical, complexes by the absence on any counter-ion. The

1 : 1 nickel complexes, formulated as CpNi(dithiolene), are very attractive in that respect since these formally d⁷ Ni(III) neutral species are expected to be paramagnetic, as indeed reported for CpNi(tfd) (tfd = 1,2-bis(trifluoromethyl)ethylene-1,2-dithiolate) where a magnetic moment of 1.67 $\mu_{\rm B}$ at room temperature was reported.¹⁷ More recently, Faulmann et al. reported the serendipitous formation of CpNi(dmit) from the reaction of NaNi(dmit)₂ with (Cp₂Ni)(BF₄) in attempts to prepare [Cp₂Ni][Ni(dmit)₂] but without mention of a possible paramagnetism.¹⁸ Considering that the absence of counter-ions in these formally d⁷ neutral radical species could also favour strong intermolecular interactions in the solid state as observed in the d¹ Cp₂M(dithiolene)^{+•} or CpM(dithiolene)₂[•] complexes, we decided to investigate more closely these attractive series and describe here syntheses, electrochemical characterizations, electronic (DFT) and solid state (single-crystal X-ray diffraction) structures and magnetic properties of three complexes with a similar dithiolene backbone, namely CpNi(dmit), CpNi(dsit) (dsit = 1,3-dithiole-2-thione-4,5-diselenolate) and CpNi(dmid). (dmid = 1,3-dithiole-2-one-4,5-dithiolate). In the two last complexes, the all-sulfur dmit ligand is replaced by the seleniumcontaining dsit or oxygen-containing dmid ligands in order to also evaluate the role of these atom substitutions on their solidstate and magnetic properties.

Results and discussion

CpNi(dmit)[•] had been obtained¹⁸ from the reaction of the nickelocenium salt (Cp₂Ni)(BF₄) with the sodium salt of the square-planar [Ni(dmit)₂]⁻ complex as the sole isolated product in attempts to prepare [Cp₂Ni][Ni(dmit)₂]. The latter reaction demonstrated however that nickelocenium was a suitable equivalent of CpNi²⁺ fragment through Cp⁻ displacement in meta-thetical reactions with dithiolate ligands. The reaction described with [Ni(dmit)₂]⁻ involved the crude monoanionic complex, as sodium salt. We investigated the reaction of (Cp₂Ni)(BF₄) with isolated *n*-Bu₄N⁺ salts of [Ni(dmit)₂]⁻ and [Ni(dmid)₂]⁻ (Scheme 1) and found that the corresponding CpNi(dmid)⁺ was obtained only in a impure form and low yield.

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[†] Electronic supplementary information (ESI) available: Table S1: Geometry optimized coordinates of CpNi(dmit)[•] derived by DFT calculations. Table S2: Selected eigenvalues of orbitals of CpNi(dmit)[•], calculated using the geometry optimized coordinates. See http://www.rsc. org/suppdata/dt/b4/b418756n/



Scheme 1

Looking for an alternative method applicable to a variety of dithiolate ligands which could avoid the systematic preparation of the oxidized [Ni(dithiolene)₂]⁻ complex for each desired dithiolate, we tried, but without success, the direct reaction of $(Cp_2Ni)(BF_4)$ with Na₂(dmit). This failure could indicate that an oxidized complex such as the monoanionic $[Ni(dmit)_2]^-$ was necessary to avoid a concurrent oxidation of the dithiolate ligand by the strongly oxidizing nickelocenium salt. An alternative to Na₂(dmit) can be offered by neutral complexes such as Cp₂Ti(dmit) or Bu₂Sn(dmit) which are known to react as dithiolene transfer reagents¹⁹ in a controlled way in the presence of oxidizing agents such as phosgene²⁰ or thiophosgene.²¹ Indeed, reaction of Bu₂Sn(dmid)²² with (Cp₂Ni)(BF₄) afforded the expected CpNi(dmid) complex but in low yield. Looking for a possibly more reactive neutral dithiolate derivative, we then considered the recently described neutral antimony complexes such as PhSb(dmit) or PhSb(dmid).23,24 PhSb(dsit) was still unknown and has been prepared from (Me₄N)₂(dsit) and PhSbCl₂. PhSb(dmit) and PhSb(dsit) were found to react with (Cp2Ni)BF4, affording CpNi(dmit) and CpNi(dsit) in moderate yields. All three radical complexes are air-stable, dark green crystalline solids, soluble in halogenated solvents.

IR spectroscopy can be an efficient tool to evaluate the degree of charge transfer on the dithiolate ligand since these complexes can be described either as a Ni(III) [CpNi^{III}]²⁺(dithiolene)²⁻, a Ni(II) [CpNi^{II}]⁺(dithiolene)⁻⁻ species or in an intermediate state. As seen in Table 1, the C=C absorption of the dithiolene ligand is particularly sensitive to the oxidation state of the complexes since it is observed at lower frequencies in the oxidized salts. The values observed here for the three CpNi(dithiolene) complexes are close to those observed in the neutral, square-planar nickel complexes, implying that the formal description of these complexes would be close to the [CpNi^{II}]⁺(dithiolene)⁻⁻ description, with the radical essentially localized on the dithiolene moiety.

Cyclic voltammetry experiments (Fig. 1 and Table 2) performed in CH_2Cl_2 show that the three radicals exhibit a quasi-reversible reduction wave to the anionic Ni(II) species, $CpNi(dithiolene)^-$, as well a quasi-reversible oxidation wave to the cationic $CpNi(dithiolene)^+$ species with peak-to-peak potential differences ($\approx 100 \text{ mV}$) larger than expected for reversible one-electron transfer processes. The reversibility and

Table 1 Characteristic IR spectral data

	C=C	C–S	C=S(O)	Ref.
$\begin{array}{c} CpNi(dmit)^{\bullet}\\ Ni(dmit)_{2}^{0.29-}\\ Ni(dmit)_{2}^{-}\\ CpNi(dsit)_{2}^{-}\\ Ni(dsit)_{2}^{-}\\ Ni(dsit)_{2}^{-2-}\\ CpNi(dmid)^{0.5-}\\ Ni(dmid)_{2}^{0.5-}\\ Ni(dmid)_{2}^{-}\\ Ni(dmid)_{2}^{-2-}\\ Ni(dmid)_{2}^{2-}\\ \end{array}$	1260 1260 1353 1440 1323 1375 1430 1398 1479 1478 1474	879, 901 890 902 885, 917 892, 980 896, 978 885, 1023	1048 1051 1052 1046 1009, 1045 1020, 1040 1024, 1040 1618, 1675 1616, 1672 1618, 1669 1601, 1641	This work 25–27 25–27 25–27 This work 28 This work 29 30 31

Table 2	Electrochemical data (<i>n</i> -Bu ₄ NPF ₆ 0.1 M in CH ₂ Cl ₂ , values in
V vs. Fc ⁺	/Fc). Values in parentheses refer to the peak-to-peak potential
difference	e. expressed in mV

	$E^{1/2}(-1/0)$	$E^{1/2}(0/+1)$
CpNi(dmit)•	-0.71 (100)	+0.28 (100)
CpNi(dsit)•	-0.72 (100)	+0.28 (100)
CpNi(dmid)•	-0.80 (110)	+0.26 (95)



Fig. 1 Cyclic voltammogram of CpNi(dmid) in CH₂Cl₂.

exact electron count on the two redox processes was ascertained with the most soluble CpNi(dmid) complex thanks to a thin layer cyclic voltammetry (TLCV) experiment,^{32,33} in the presence of an equimolar amount of ferrocene as reference. As seen in Fig. 2, the reversibility of both oxidation and reduction processes at scan speeds as low as 5 mV s⁻¹ is demonstrated from the symmetry of each process. Furthermore, comparison of peak area with that observed for the Fc/Fc⁺ couple confirms that both redox processes involve one-electron transfers.



Fig. 2 Cyclic voltammetry of CpNi(dmid) under TLCV conditions in 1 mM concentration in CH_2Cl_2 with *n*-Bu₄NPF₆ 0.25 M.

Molecular and electronic structures

The X-ray crystal structure of CpNi(dmit)[•] has been already described by Faulmann *et al.*¹⁸ and was re-determined only for comparison purposes. CpNi(dsit)[•] was found to be isostructural

with CpNi(dmit)[•]. It crystallizes in the monoclinic system, space group $P2_1$, with one molecule in a general position in the unit cell (Fig. 3). The NiSe₂C₂ metallacycle is planar (largest deviation 0.04(3) Å) and is essentially perpendicular to the Cp ring (85.4(4)°).



Fig. 3 ORTEP view of CpNi(dsit)[•]. Thermal ellipsoids are drawn at 50% probability level.

The comparison of the intramolecular Ni-Se, Se-C and C=C bond distances in CpNi(dsit) with other dsit complexes such as [Ni(dsit)₂]²⁻ and [Ni(dsit)₂]^{•-} is difficult since no structural data are available for the dianioinic [Ni(dsit)₂]²⁻ species while the radical anion species is dimerised in the solid state,³⁴ with one selenium atom entering the coordination sphere of the nickel atom of the neighbouring complex. Proper comparisons can be obtained however from the structural characteristics of the Ni(dsise)₂^{2-,•-} complexes (dsise = 1,3-dithiole-2-selone-4,5diselenolate) which exhibit a similar Ni-Se coordination scheme. Both the di- and monoanion³⁵ have been characterized in the solid state as monomers. As shown in Table 3, the shortening of the Ni-Se and Se-C bonds in CpNi(dsit) when compared with the reduced [Ni(dsise)₂]²⁻ or [Ni(dsise)₂]⁻⁻ species also indicate the large contribution of the dithiolene moiety in the SOMO (singly occupied molecular orbital) of the complex.

As seen in Table 4, similar trends are observed in the molecular structure of CpNi(dmid) which crystallizes in the orthorhombic system, space group *Pnma*. The molecule is located on a mirror plane which includes the Ni(dmid) moiety while the Cp ring is disordered on two positions related by the same mirror plane (Fig. 4). The NiS₂C₂ metallacycle is fully planar by symmetry and is essentially perpendicular to the Cp ring (88.3(4)°). As already noted in CpNi(dsit), the evolution of the bond distances within the metallacycle as well as the characteristic IR frequencies (Table 1) points for a oxidized dithiolate ligand, that is close to a Ni(II) [CpNi^{II}]⁺[dithiolene⁻] description.

In order to check this assumption, we have performed theoretical calculations on CpNi(dmit) at DFT level with the

 Table 3
 Selected intramolecular distances in CpNi(dsit)* and reference compounds

	Ni–Se/Å	Se–C/Å	C=C/Å	Ref.
CpNi(dsit)	2.250(13) 2.250(18)	1.863(21) 1.871(10)	1.359(14)	This work
Ni(dsit)2	(2.329)	(1.882)	(1.342)	34
Ni(dsise)2.	2.276	1.875	1.36	35
Ni(dsise) ₂ ²⁻	2.305	1.883	1.364	35



Fig. 4 ORTEP view of CpNi(dmid)*. Thermal ellipsoids are drawn at 50% probability level. The inset shows the disorder model in which the dotted line is the crystallographic mirror plane.

UB3LYP method³⁷ and 6-31G* basis set, aimed at optimizing its geometry and, subsequently, at generating the sequence of molecular orbitals. Characteristic calculated bond distances compare well with those observed from the X-ray crystal structure determination (Table 4) with the largest discrepancies (0.036 Å) similar to those found for the calculated geometries of dithiolene complexes such as $[Ni(S_2C_2Me_2)_2]^{0,-,2-}$.³⁸ As shown in Fig. 5, the SOMO (singly occupied molecular orbital) of CpNi(dmit) is essentially localized on the dithiolene moiety, with a small contribution of the CpNi fragment, thus confirming the spectroscopic (IR) and structural results. As a consequence, one can expect that, in the solid state, short *intermolecular* contacts between molecules which involve the dithiolene moiety, will lead to strong electronic interactions, as indeed experimentally observed from the magnetic behaviour of those radical species.



Fig. 5 Singly occupied molecular orbital (SOMO) of CpNi(dmit) (DFT-UB3LYP/6-31G*).

Solid-state structures and magnetic properties

Let us first describe the solid-state and magnetic properties of isostructural CpNi(dmit)[•] and CpNi(dsit)[•] radicals. As shown in Fig. 6, the radicals organise into layers parallel to the (a,b) plane without any stacking of the planar dithiolene moieties, an original feature of these complexes. In spite of these tilt angles,

 Table 4
 Selected intramolecular distances in CpNi(dmid)*, CpNi(dmit)* and averaged distances in reference compounds. Calculated values for CpNi(dmit)* (DFT-UB3LYP/6-31G*) are given in italics

Compound	Ni–S/Å	S–C/Å	C=C/Å	Ref.
CpNi(dmid)' CpNi(dmit)' Ni(dmit)2 ⁰ Ni(dmid)2'- Ni(dmid)2 ²⁻	2.138(1), 2.145(1) 2.138(2), 2.133(2) 2.138(2), 2.143(2) 2.163 2.147 2.152 2.194	1.718(3), 1.712(3) 1.706(8), 1.716(8) 1.716(7), 1.741(7) <i>1.742</i> 1.700 1.718 1.734	1.352(4) 1.36(1) 1.354(8) <i>1.366</i> 1.391 1.352 1.340	This work 18 This work Calc. 25 36 31

Table 5 Short intermolecular contacts between radicals in CpNi(dmit) and CpNi(dsit) and associated calculated β overlap interaction energies

	CpNi(dmit)	CpNi(dmit)			CpNi(dsit)		
Interacti	on Contact/Å		β /meV	Contact/Å		β/meV	
А	$S(1) \cdots S(2)^a$ $S(3) \cdots S(4)^a$	3.611(22) 3.737(21)	91.9	$\frac{\operatorname{Se}(1)\cdots\operatorname{Se}(2)^a}{\operatorname{S}(1)\cdots\operatorname{S}(2)^a}$	3.634(15) 3.854(14)	48.8	
В	$\frac{S(3)\cdots S(1)^{b}}{S(1)\cdots S(3)^{b}}$	4.041(6) 4.264(6)	25.1	$\frac{S(1)}{S(1)} \cdot \cdot \cdot \frac{S(2)}{S(1)^{b}}$ $\frac{S(1)}{S(1)} \cdot \cdot \cdot \frac{S(2)}{S(1)^{b}}$	4.079(5) 4.342(5)	28.9	
С	$\mathbf{S(2)} \cdots \mathbf{S(4)}^c$ $\mathbf{S(4)} \cdots \mathbf{S(2)}^c$	3.948(4) 4.041(4)	66.1	$\widehat{\operatorname{Se}(2)} \cdots \widehat{\operatorname{S}(2)}^c$ $\widehat{\operatorname{S}(2)} \cdots \widehat{\operatorname{Se}(2)}^c$	3.911(3) 4.104(3)	27.2	
D			13.3			21.4	
E			10.8			11.1	

Symmetry operations: $^{a} 1 + x, y, z. ^{b} - x, 0.5 + y, 1 - z. ^{c} - 1 - x, -0.5 + y, 1 - z.$



Fig. 6 A view of one (a,b) layer in CpNi(dsit) with intra-layer interaction A running along a and interactions B and C running along b. Dotted lines show the shortest Se \cdots Se, Se \cdots S and S \cdots S contacts between one molecule and its neighbours.

short Se \cdots Se, Se \cdots S and S \cdots S intermolecular contacts within the slabs (Table 5) are identified, giving rise to a network of intermolecular interactions noted A–C in Fig. 6.

The temperature and field dependence of the molar magnetic susceptibility for CpNi(dmit)[•] and CpNi(dsit)[•] are shown in Figs. 7 and 8, respectively, in the low-temperature regime. At the higher temperatures, both compounds exhibit a Curie–Weiss behaviour with $\theta_{dmit} = -66$ K and $\theta_{dsit} = -33$ K, the signature of the presence of strong antiferromagnetic interactions in the solid state. The susceptibility of both compounds exhibits a maximum at 43 K (dmit) and 23 K (dsit), and below a transition to an



Fig. 7 Magnetic susceptibility of CpNi(dmit) in the low-temperature regime at different fields.



Fig. 8 Magnetic susceptibility of CpNi(dsit) in the low-temperature regime at different fields.

antiferromagnetic ground state with $T_{\text{N\acute{e}el}}(\text{dmit}) = 27 \text{ K}$ and $T_{\text{N\acute{e}el}}(\text{dsit}) = 18 \text{ K}$, as demonstrated from the field dependence of the magnetic susceptibility below $T_{\text{Néel}}$ in both compounds (Figs. 7 and 8). This behaviour demonstrates that a threedimensional set of intermolecular interactions is present in both neutral radicals, as confirmed by the calculations of the extended Hückel β overlap interaction energies.³⁹ Indeed, as shown in Fig. 6 for CpNi(dsit), each radical interacts with six neighbouring molecules within the slabs (interactions A-C), and with four other molecules pertaining to parallel slabs (interactions D and E). Calculated β values are collected in Table 5 for both CpNi(dmit) and CpNi(dsit), and confirm that, (i) the strongest interactions are observed within the slabs, (ii) the interactions are stronger in CpNi(dmit), as experimentally observed from both larger Curie-Weiss and Néel temperatures.

Contrariwise to the two isostructural CpNi(dmit)[•] and CpNi(dsit)[•], the organisation of CpNi(dmid)[•] into slabs (Fig. 9) only holds from a structural point of view since short $S \cdots S$



Fig. 9 A view of the slabs of CpNi(dmid)' developing parallel to the (a,b) plane with interacting molecules within columns along b.

distances are found only within stacks running along b where one recovers the more usual face-to-face stacking of the dithiolene moieties.

The temperature dependence of the magnetic susceptibility of CpNi(dmid)' shown in Fig. 10 does not exhibit any field dependence but still a Curie-Weiss behaviour in the higher temperatures with $\theta_{\text{dmid}} = -55$ K, demonstrating again the occurrence of strong antiferromagnetic interactions. The presence of a susceptibility maximum at 32 K with a decrease to almost zero at the lowest temperatures demonstrates that the radical species most probably become paired, suggesting a structural transition and a dimerisation. Calculations of the extended Hückel β overlap interaction energies performed on the roomtemperature X-ray crystal structure of CpNi(dmid)' show that molecules are essentially interacting along the b axis in a uniform chain ($\beta = 82$ meV) while all other intermolecular interactions are much weaker (< 15 meV). As a consequence, a uniform chain model was used to fit the magnetic susceptibility data in the high-temperature regime (Fig. 10), affording a J/k value of -44 K. Most probably, this uniform chain experiences a dimerisation around 32 K, leading to a diamagnetic ground state.



Fig. 10 Temperature dependence of the magnetic susceptibility of CpNi(dmid).

In summary, we have first confirmed here that the neutral CpNi(dithiolene) complexes are indeed paramagnetic, as anticipated by King forty years ago.¹⁷ The synthetic procedure reported by Faulmann has been improved albeit other routes still warrant exploration. These attractive radical complexes are stable in a wide 1 V redox range and their electrochemical properties can most probably be varied by modifying the substituents on the dithiolate ligand. We have also shown by a combination of structural and spectroscopic data, and theoretical investigations that most of the radical is delocalized on the dithiolene ligand, an issue of strong interest in the prospect of building magnetic materials since efficient intermolecular interactions can be anticipated. Indeed, the two isostructural CpNi(dmit) and CpNi(dsit) are characterized by a three-dimensional set of intermolecular interactions which does not involve the otherwise recurrent face-to-face overlap between the planar dithiolene moieties. This original solidstate organisation leads to an ordered antiferromagnetic ground state at low temperature, thus demonstrating that the absence of any counter-ions in these neutral radical species allows indeed for extended intermolecular interactions and for an ordered magnetic ground state. On the other hand, CpNi(dmid). provides an illustrative counter-example where the face-toface overlap of the dmid moieties drives the formation of magnetic chains prone to dimerisation. Further work within these CpNi(dithiolene). series will focus on more electron-rich dithiolate ligands for investigating possibly conducting mixedvalence CpNi(dithiolene)[•]/CpNi(dithiolene)⁺ salts as well as on functional dithiolate ligands able to further favour intermolecular interactions through hydrogen or halogen bonding.⁴⁰

Experimental

General

The syntheses of the complexes were carried out under nitrogen, using standard Schlenk techniques. Dry CH_2Cl_2 and CH_3CN were obtained by distillation over P_2O_5 , and THF was distilled over sodium and benzophenone. Elemental analyses were performed by the "Service d'Analyse du CNRS" at Gif/Yvette, France. (Cp_2Ni)BF₄ was prepared according to a described procedure⁴¹ from commercial Cp_2Ni (Strem Chemicals) and (Cp_2Fe)BF₄.

CpNi(dmit)[•].

From $(n-Bu_4N)[Ni(dmit)_2]$. To a solution of $(Cp_2Ni)BF_4$ (80 mg, 0.29 mmol) in dry CH₃N (5 mL) was added a suspension of $(n-Bu_4N)[Ni(dmit)_2]$ (200 mg, 0.29 mmol) in CH₃CN (10 mL) and the reaction mixture stirred for 2 h. Solvent was then removed under vacuum and the remaining dark green solid Soxhlet extracted with CH₂Cl₂. Concentration of the green CH₂Cl₂ solution, filtration on a short SiO₂ column and concentration of the CH₂Cl₂ solution afforded CpNi(dmit) as green crystals, yield 44 mg (47%).

From PhSb(dmit). To a solution of $(Cp_2Ni)BF_4$ (100 mg, 0.36 mmol) in CH₃CN (5 mL) was added a solution of PhSb(dmit) (123 mg, 0.31 mmol) in dry THF (15 mL). The solution was stirred overnight, evaporated and the solid extracted with CH₂Cl₂, the solution was filtered on a short SiO₂ column and the concentrated solution layered with MeOH. Yield 25 mg (26%). v_{max}/cm^{-1} 3500br s, 3090s (C–H), 2057m, 1796m, 1438s (C=C, Cp), 1400s (C=C, Cp), 1380s (C=C, Cp), 1260s (C=C), 1015s and 1048s (C=S), 901s and 879s (C–S). Found: C, 30.15, H, 1.63. C₈H₅NiS₅ requires C, 30.01; H, 1.57%.

PhSb(dsit). A solution of dsit(COPh)₂ (1 g, 2 mmol)⁴² in THF (60 mL) was treated with a solution of Me₄NOH (2.91 g 25 wt% in MeOH, 8 mmol) in THF (10 mL). A violet precipitate of (Me₄N)₂(dsit) was formed within a few minutes and, after 1 h of stirring, the precipitate was filtered off under nitrogen in order to eliminate the (PhCOO)⁻(NMe₄)⁺ salt still soluble. Then, the diselenolate was dispersed in THF (40 mL) and dichlorophenylstibine43 (0.54 g, 2 mmol) in THF (10 mL) was rapidly added. The resulting deep red solution was stirred overnight and then filtered through Celite in order to remove the precipitated Me₄NCl. After evaporation of almost all the solvent, precipitation upon addition of pentane, filtration on a glass frit, washing of the resulting powder with methanol, then with pentane and finally drying under vacuum, PhSb(dsit) was recovered as a deep red solid. Yield 0.5 g (51%). v_{max}/cm^{-1} : 1479m (C=C), 1430 (C=C), 1056s (C=S), 1024s (C=S), 947m (C-S), 733m (C₆H₅), 693m (C₆H₅), 509m, 449m (C₆H₅). Found: C, 21.87, H, 1.15. C₉H₅S₃Se₂Sb requires C, 22.11; H, 1.03%.

CpNi(dsit). To a solution of $(Cp_2Ni)BF_4$ (137 mg, 0.5 mmol) in CH₃CN (10 mL) was added a solution of PhSb(dsit) (244 mg, 0.5 mmol) in THF (10 mL). After stirring for 2 h, the dark precipitated solid was filtered off and recrystallized from hot toluene to afford CpNi(dsit) as dark plates. Yield 75 mg (36%). v_{max}/cm^{-1} : 3500br s, 3087s (C–H), 1619m, 1402s (C=C, Cp), 1434m (C=C, Cp), 1323m (C=C), 1009s, 1045s (C=S), 892s (C–S). Found: C, 22.77, H, 1.19. $C_8H_5NiS_3Se_2$ requires C, 23.22; H, 1.22%.

CpNi(dmid)[•].

From $(n-Bu_4N)[Ni(dmid)_2]$. To a solution of $(Cp_2Ni)BF_4$ (138 mg, 0.5 mmol) in dry CH₃N (10 mL) was added a suspension of $(n-Bu_4N)[Ni(dmid)_2]$ (330 mg, 0.5 mmol) in

Table 6 Crystallographic data

Compound	CpNi(dmid)•	CpNi(dmit)*	CpNi(dsit)*
Formula	C ₈ H ₅ NiOS ₄	C ₈ H ₅ NiS ₅	C ₈ H ₅ NiS ₃ Se ₂
FW	304.07	320.13	413.93
Crystal system	Orthorhombic	Monoclinic	Monoclinic
Space group	Pnma	$P2_1$	$P2_1$
a/Å	8.0485(7)	5.9185(14)	6.0750(12)
b/Å	7.2993(7)	7.9334(12)	7.9798(11)
c/Å	17.787(2)	11.732(3)	11.8369(19)
β/°	_ ``	97.86(3)	97.55(2)
$U/Å^3$	1044.97(18)	545.7(2)	568.85(16)
T/K	293(2)	293(2)	293(2)
Z	4	2	2
μ/mm^{-1}	2.613	2.685	8.607
Total refls.	5997	4152	4282
Unique refls. (R_{int})	1075 (0.0357)	1949 (0.0772)	2090 (0.0792)
Unique refls. $(I > 2\sigma(I))$	823	1101	1475
$R_1, wR_2 (I > 2\sigma(I))^a$	0.0263, 0.0585	0.0386, 0.0580	0.0382, 0.0743
R_1, wR_2 (all data) ^a	0.0394, 0.0615	0.0952, 0.0687	0.0669, 0.0805

CH₃CN (20 mL) and the reaction mixture stirred for 3 h. Solvent was then removed under vacuum and the remaining dark green solid extracted with CH_2Cl_2 . Concentration of the green CH_2Cl_2 solution, filtration on a short SiO₂ column, concentration of the CH_2Cl_2 solution and layering with pentane afforded CpNi(dmid)[•] as green crystals, yield 18 mg (12%).

From PhSb(dmid). To a solution of $(Cp_2Ni)BF_4$ (140 mg, 0.5 mmol) in CH₃CN (10 mL) was added a solution of PhSb(dmid) (190 mg, 0.5 mmol) in dry THF (20 mL). The solution was stirred for 2 h, evaporated and the solid extracted with CH₂Cl₂. The solution was filtered on a short SiO₂ column and the concentrated solution layered with MeOH. Yield 9 mg (6%). v_{max}/cm^{-1} : 3500br s, 3107s (C–H), 1675s (C=O), 1618s (C=O), 1438s (C=C, Cp), 1397s (C=C, Cp), 1276m (C=C). Found: C, 35.02, H, 2.03. C₈H₅NiOS₄ requires C, 31.60; H, 1.66%.

Electrochemistry

Cyclic voltammetry experiments were performed on a VPM potentiostat in dried CH_2Cl_2 solutions of 0.05 M *n*-Bu₄NPF₆ as electrolyte at room temperature, at a scan rate of 100 mV s⁻¹. A Pt working electrode (diameter 1 mm), a Pt counter-electrode and a Ag/AgNO₃ reference electrode were used. Under those conditions, the ferrocene–ferrocenium wave was observed at $E^{1/2} = 0.20$ V. Thin layer cyclic voltammetry (TLCV) experiments were performed in a dry box in 1 mM CH₂Cl₂ solutions of product and 0.25 M *n*-Bu₄NPF₆ as electrolyte *vs*. ferrocene–ferrocenium couple.

Theoretical calculations

DFT calculations were performed on CpNi(dmit)[•] with the UB3LYP method³⁷ and 6-31G^{*} basis set using Gaussian03 software.⁴⁴ Initial geometry was taken from the X-ray crystal structure. Calculations of the intermolecular β overlap interactions energies were performed with the extended Hückel method.⁴⁵ A modified Wollsberg–Helmholtz formula was used to calculate the $H_{\mu\nu}$ non-diagonal values.⁴⁶ Single- ζ orbitals were used for all atoms except nickel.

X-Ray crystallographic analysis

Crystals were mounted on top of a thin glass fibre. 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 (T = 293(2) K). The crystal data are summarized in Table 6. Structures were solved by

direct methods (SHELXS-97) and refined (SHELXL-97) by fullmatrix least-squares methods. Absorption corrections were applied. Hydrogen atoms were introduced at calculated positions (riding model), included in structure factor calculations, and not refined.

CCDC reference numbers 258291-258293.

See http://www.rsc.org/suppdata/dt/b4/b418756n/ for crystallographic data in CIF or other electronic format.

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