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Chiral, Neutral, and Paramagnetic Gold Dithiolene Complexes Derived from Camphorquinone

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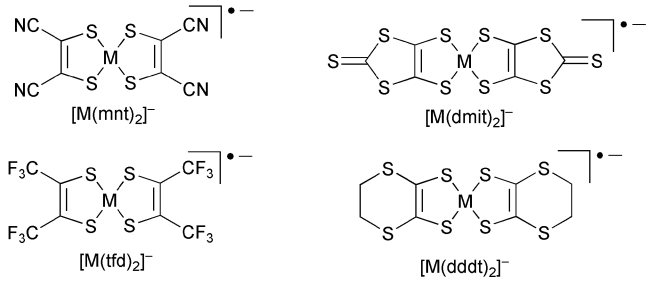
Reaction of racemic (DL)- or enantiopure (D)-camphorquinone with P_4S_{10} in dimethylimidazolidinone followed by addition of $NiCl_2{\cdot}6H_2O$ or $KAuCl_4$ affords the corresponding bornylenedithiolato metal complexes [(DL-bordt)$_2$Ni], [(D-bordt)$_2$Ni], [(DL-bordt)$_2$Au], and [(D-bordt)$_2$Au] in their neutral form. Cyclic voltammetry and UV/Vis/NIR spectrometry show that the bornylenedithiolato ligand acts as a highly electron-rich dithiolene ligand. Complete assignment of the ^{1}H and ^{13}C NMR signals of the diamagnetic enantiopure [(D-bordt)$_2$Ni] is reported thanks to a combination of 2D NMR spectroscopy experiments. X-ray crystal structure determinations were performed for the four complexes, showing that the two diastereomeric mixtures, [(DL-bordt)$_2$Ni] and [(DL-bordt)$_2$Au], are isomorphous (space group $P2_1/c$), as are also the two enantiopure complexes, [(D-bordt)$_2$Ni] and [(D-bordt)$_2$Au] (space group $P2_1$). Positional disorder of the two (D)- and (L)-bornylenedithiolate enantiomers on the same position is observed in the structure of the diastereomeric mixtures, with the complex located on the inversion center. The temperature dependence of the magnetic susceptibility of the paramagnetic gold complexes [(DL-bordt)$_2$Au] and [(D-bordt)$_2$Au] demonstrates the presence of antiferromagnetic interactions, to a larger extent in the diastereoisomeric mixture [(DL-bordt)$_2$Au] than in the enantiopure complex [(D-bordt)$_2$Au], as a consequence of stronger lateral S···S intermolecular interactions in the former.

Introduction

Introduction of chirality into molecular conducting materials is currently actively investigated with the hope of observing specific effects such as the electrical magneto-chiral anisotropy effect predicted by Rikken[1] and already observed in chiral nanotubes,[2] or a chiral Hall effect.[3] As pointed out by Avarvari and Wallis in their recent review on this topic,[4] most of the activity in this research area has concentrated on the elaboration of chiral tetrathiafulvalene (TTF) salts, which can be addressed in two different ways. The first route implies the synthesis of chiral TTFs for further electrocrystallization in the presence of a variety of anions; the second route involves chiral anions engaged in the electrocrystallization experiments with achiral TTF derivatives. Both approaches have already afforded several chiral salts with metallic conductivity, based for example on dimethyl or tetramethyl BEDT-TTF,[5] TTF oxazoline donor molecules,[6,7] or chiral counterions such as antimony tartrate.[8]

Dithiolene complexes[9] offer an attractive alternative to TTF derivatives for the elaboration of conducting or magnetic compounds. Formally d^7 radical complexes such as $[M(mnt)_2]^{-\cdot}$ or $[M(tfd)_2]^{-\cdot}$ (M = Ni, Pd, Pt) (Scheme 1) have been extensively engaged in the elaboration of magnetic solids[10] with closed-shell or open-shell[11,12] cations, but also as metalloligands in polymetallic systems.[13] On the other hand, $[M(dmit)_2]^{-\cdot}$ or $[M(dddt)_2]^{-\cdot}$ (M = Ni, Pd, Pt) can be partially oxidized into mixed-valence conducting and eventually superconducting salts.[14]



Scheme 1. Structure of paramagnetic dithiolene complexes.

In this respect, the introduction of chirality into paramagnetic dithiolene complex salts offers many attractive perspectives for the elaboration of chiral magnetic or con-

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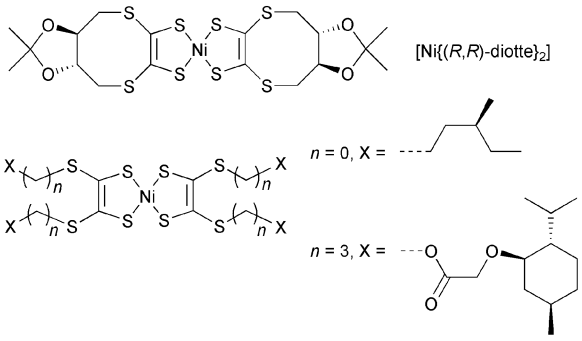
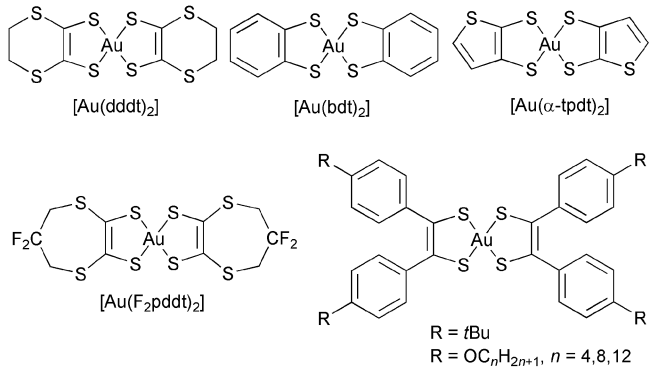
ducting materials. However, one single example has been reported so far, $[Ni(diotte)_2]^{-1,0}$ (Scheme 2), isolated as optically pure (*SS*) and (*RR*) enantiomers for co-crystallization with chiral viologens to form diastereomeric and enantiomeric ion-pair complexes.[15] The conductivity of diastereomeric complexes was shown to differ by one to two orders of magnitude, but the lack of crystals big enough for X-ray crystal structure determination limited the rationalization of these results.



Scheme 2. Examples of chiral nickel dithiolene complexes, as reported by Kisch[15] or Marshall.[18]

Besides these anionic radical complexes, the oxidized, formally d^6, neutral, and diamagnetic nickel dithiolene complexes are also currently intensively investigated for several applications such as laser dyes,[16,17] dyes for liquid crystal devices,[18] light compensation filters for near-infrared (NIR) radiation, optical recording disks,[19] or as semiconductors for field-effect transistors.[20] The essential molecular characteristics of the neutral complexes used in these devices are their excellent thermal stability and their strong NIR absorption, found at wavelengths ranging from 0.8 up to 1.5 μm. Earlier work by Giroud, Müller-Westerhoff,[21] and Ohta[22] has also demonstrated that these complexes could exhibit several thermotropic phases, while Marshall demonstrated that their good solubility in liquid crystal hosts allows high NIR dye concentrations without reducing the liquid crystal order parameter.[18] Here again, the introduction of chirality has been scarcely addressed, with one single report by Marshall who described several neutral chiral nickel dithiolene complexes and demonstrated that they were also capable of inducing a chiral nematic phase when dissolved into a nematic liquid crystal host.[18]

Gold dithiolene complexes offer an attractive variation between the two groups of (Ni, Pd, Pt) complexes evoked above, that is the formally d^7 paramagnetic (S = ½) anions on the one hand, the formally d^6 low-spin (*S* = 0) neutral complexes on the other hand. Indeed, the anionic d^8 Au^{III} $[Au(dithiolene)_2]^-$ species can be oxidized into stable neutral radical form $[Au(dithiolene)_2]^{\cdot}$, which can thus combine the paramagnetism of open-shell (S = ½) complexes with the solubility and liquid crystal behavior of neutral complexes. However, only a few neutral gold dithiolene complexes have been reported so far, either as insoluble crystalline, eventually conducting, materials in $[Au(dddt)_2]$,[23] $[Au(bdt)_2]$,[24] $[Au(F_2pdt)_2]$,[25] or $[Au(\alpha\text{-tpdt})_2]$[26] (Scheme 3), or as soluble radical derivatives in $[Au\{S_2C_2(p\text{-}t\text{BuPh})_2\}]$[27] or $[Au\{S_2C_2(p\text{-}OC_nH_{2n+1}Ph)_2\}]$.[28]



Scheme 3. Neutral open-shell gold dithiolene complexes.

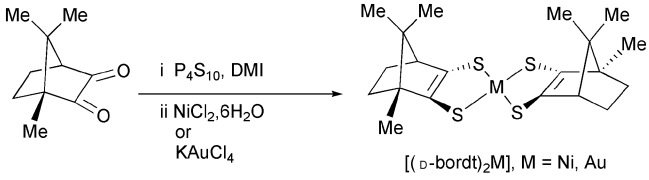
We report here the synthesis and structural, electrochemical, and magnetic characterization of the first chiral radical neutral gold dithiolene complexes. Furthermore, the source of chirality here is the easily available camphor derivatives. Indeed, a recent patent[29] described that the sulfidizing of the reduced α-hydroxy camphor, followed by reaction with a group 10 metal (Ni, Pd, Pt) salt, afforded the corresponding bornylenedithiolene neutral complex $[(DL\text{-bordt})_2Ni]$ as a diastereomeric mixture of $[(D\text{-bordt})_2Ni]$, $[(L\text{-bordt})_2Ni]$, and the *meso* form [(D-bordt)(L-bordt)Ni]. The reported strong solubility and volatility of these complexes and their high absorption in the range 750–850 nm make them very useful for optical recording media. Other claims involved their use as antioxidants, stabilizers, corrosion inhibitors, or as protective layers for colored photographic layers. On the other hand, the chiral character of the starting material, and that of the corresponding metal complexes was not specifically addressed in this patent. On the basis of this report, we wanted to fully characterize these attractive nickel complexes and investigate whether the analogous but paramagnetic gold complexes could be prepared. Of further interest was the possibility of a differential magnetic behavior in the solid state, between the enantiopure $[(D\text{-bordt})_2Au]^{\cdot}$ and the diastereomeric $[(DL\text{-bordt})_2Au]^{\cdot}$ mixture, as discussed below.

Results and Discussion

Syntheses

The preparation of alkyl or aryl-substituted nickel dithiolene complexes is most often based on the sulfidizing of 1,2-diketones or α-hydroxy ketones with P_4S_{10}, B_2S_3, or Lawesson's reagent in dioxane.[30] Based on a recent report,[31] we have also described that the use of DMI (DMI:

dimethylimidazolidinone) rather than dioxane as the reaction solvent allowed a strong increase in the yield of the reaction of 1,2-diketones with P_4S_{10} to give the neutral nickel dithiolene complexes.[28] Since the sulfidizing of α-hydroxy camphor with P_4S_{10} in dioxane has been reported to afford the corresponding Ni complex [(DL-bordt)$_2$Ni] in good yield,[29] we investigated a similar reaction starting directly from the camphorquinone (bornanedione) rather than the reduced α-hydroxy camphor and performed the reaction in DMI rather than in dioxane. Following this route (Scheme 4), the bornylenedithiolatonickel complex [(DL-bordt)$_2$Ni] was obtained in good yield (ca. 75%) after chromatographic purification.



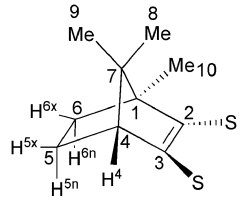
Scheme 4. Synthetic procedure for the enantiopure [(D-bordt)$_2$M], M = Ni, Au.

The reaction was conducted on the racemic DL-camphorquinone and on the enantiopure D-camphorquinone, affording the diastereomeric mixture [(DL-bordt)$_2$Ni] and the enantiopure [(D-bordt)$_2$Ni], respectively, with comparable yields (≈ 75%).

Only very few examples of neutral radical gold dithiolene complexes have been reported in the literature.[23–28] They are most often based on the chemical or electrochemical oxidation of the corresponding anionic and diamagnetic Au^{III} dithiolene complexes $[Au(dt)_2]^-$. The latter are easily obtained from the corresponding dithiolate and a Au^{III} salt such as $AuCl_4^-$. In the present case, the isolated bornylenedithiolato ligands are not available. Therefore, the sulfidizing procedure described above for the nickel derivatives has been successfully expanded here to the gold complexes, with $KAuCl_4$ as the metal source. The radical complexes [(DL-bordt)$_2$Au] and [(D-bordt)$_2$Au] were obtained in a lower yield of 25–35%. The four complexes are very soluble in organic solvents such as hexane, ethyl ether, dichloromethane, or acetone. Thus, the nickel complexes have been successfully crystallized by slow diffusion of MeOH into a CH_2Cl_2 solution, while the gold complexes were crystallized by the slow evaporation of the solvent from an Et_2O solution.

NMR Spectroscopic Studies: An Intricate Situation

The ^{1}H NMR spectra of camphor derivatives are particularly complex to analyze, and these compounds have provided in the past a convenient model for a variety of NMR spectroscopic investigations[32] and still continue to hold the attention of numbers of research groups.[33] Indeed, despite the fact that camphor derivatives have been known for some decades, the assignment of the proton spectrum of camphor has been the subject of some controversy in the literature.[33b,34] We will describe here the assignments of the ^{1}H and ^{13}C NMR spectra of [(DL-bordt)$_2$Ni] together with that of camphorquinone, which was used as reference compound. The numbering system adopted for these assignments is given in Scheme 5.[35]



Scheme 5. Numbering scheme for the bornylenedithiol moiety in [(D-bordt)$_2$Ni].

The assignment of the signals of [(D-bordt)$_2$Ni] has been performed by a combination of 2D NMR spectroscopy experiments: HMBC (Heteronuclear Multiple Bond Correlation), HMQC (Heteronuclear Multiple Quantum Coherence), ^{1}H/^{1}H COSY (Correlation spectroscopy) and ^{1}H homonuclear decoupling experiments. In the ^{1}H NMR spectrum, H^4 (δ = 3.1 ppm) appears as a narrow doublet due to vicinal coupling to H^{5x} (δ = 2.12/2.03 ppm, $^3J_{H^4\text{-}H^{5x}}$ = 4.1 Hz), but no coupling was observed with the *endo* proton H^{5n}. It is known for camphor that the $^3J_{H^4\text{-}H^{5x}}$ and $^3J_{H^4\text{-}H^{5n}}$ vicinal couplings lie around 3–4 Hz and 0–2 Hz, respectively, in accordance with our assignment for H^{5x}.[35] The assignment of H^{5x} vs. H^{5n} may be also confirmed with the determination of the dihedral angles obtained from the X-ray diffraction data (vide infra). Indeed, the relationship between the dihedral angle and the vicinal coupling is approximated by the original Karplus equation, $^3J = A + (B \times \cos\phi) + (C \times \cos 2\phi)$, where ^3J is the coupling constant, ϕ is the dihedral angle, and A, B and C are constants (A = 4.22, B = –0.5, C = 4.5).[36] From X-ray diffraction data, the dihedral angles are 44° for (H^4–C–C–H^{5x}) and 77.6° for (H^4–C–C–H^{5n}), affording the theoretical coupling constants $^3J_{H^4\text{-}H^{5x}} \approx 4.02$ Hz and $^3J_{H^4\text{-}H^{5n}} \approx 0.03$ Hz, in accordance with the experimental measurements (vide supra). As already observed by Rittner et al.[37] for *endo*-3-halosubsituted camphors, second-order signals are observed for H^5 and H^6. The multiplet recorded at 1.30/1.24 ppm was assigned to H^{5n}/H^{6n}, since two different cross peaks were detected in the HMQC experiment, the same as those observed for H^{5x}/H^{6x} (Figure 1, top).

The signals of H^{5n} and H^{6n} appear to be fully overlapping, and no exact assignment was achieved. H^{6x} (δ = 1.88/1.80 ppm) was finally assigned by means of ^{1}H homonuclear decoupling experiments. Indeed, after irradiation at the resonance frequency of H^{5n}/H^{6n}, a narrow doublet of doublet is obtained for H^{5x} and a doublet is obtained for H^{6x} with a $^3J_{H^{5x}\text{-}H^{6x}}$ of 9.4 Hz, in accordance with typical "*exo*/*exo*" literature values for camphor derivatives (Figure 1, bottom).[35] After determining the dihedral angle

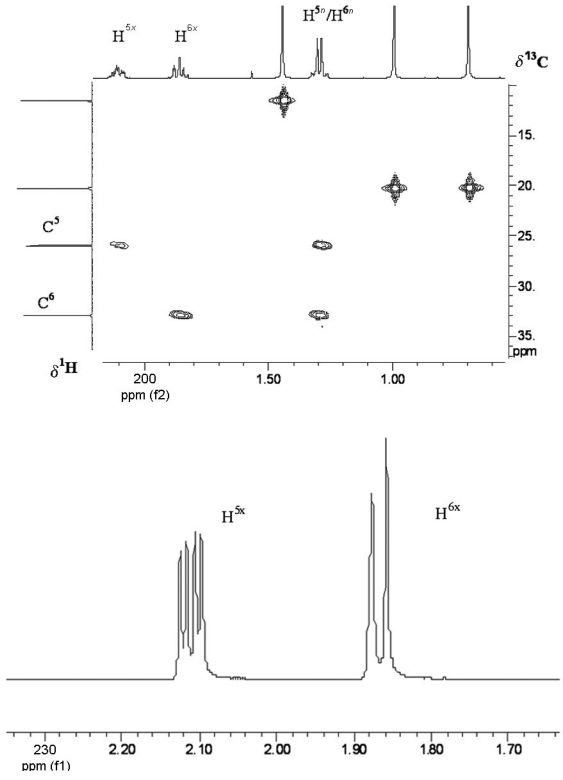


Figure 1. Top: portion of the HMQC ($CDCl_3$) spectrum of [(D-bordt)$_2$Ni]. Bottom: portion of the ^{1}H NMR spectrum ($CDCl_3$) of [(D-bordt)$_2$Ni] after irradiation at the resonance frequency of H^{5n}/H^{6n}.

(H^{5x}–C–C–H^{6x}), 1°, obtained from X-ray diffraction data, we evaluated the theoretical coupling constant, $^3J_{H^{5x}\text{-}H^{6x}}$ = 8.2 Hz. Thus, the theoretical coupling constant appears to be in accordance with the experimental value, but it is slightly lower due to the dihedral angle, which is almost 0°.[38] Similarly, a coupling constant of $^3J_{H^{5x}\text{-}H^{6n}} \approx 2.5$ Hz is predicted for a dihedral angle (H^{5x}–C–C–H^{6n}) of 122.2°. In terms of chemical shifts, H^4 appears to be deshielded relative to H^5 and H^6, as a result of the proximity of the metallacycle. Some long-range couplings were also detected in COSY experiments, for example, those of H^9/H^8 ("W" coupling) or H^4 with the three methyl groups.[37] The assignment of H^8 and H^9 appeared to be difficult to achieve. This assignment was thus performed by means of the slight cross peak observed in the COSY experiment between H^8 and H^{5n}/H^{6n}, as already reported.[37] However, complementary experiments[39] need to be performed in order to achieve this last assignment with complete certitude. In the HMBC experiments, C^6 (δ = 32.9 ppm) displays a cross peak with H^{10} (δ = 1.42 ppm), but it does not have a cross peak with H^9 or H^8. Note also that, despite the presence of the nickel atom and the two bornane moieties, the ^{1}H NMR spectrum of complex [(D-bordt)$_2$Ni] appears to be very similar to the camphorquinone spectrum; H^4 and H^{10}, however, are deshielded by approximately 0.4/0.5 ppm, highlighting the effect of the metallacycle in comparison to the two carbonyl functions (Table 1).

Table 1. ^{1}H and ^{13}C chemical shift data for [(D-bordt)$_2$Ni], camphorquinone and camphor (all data in ppm, in $CDCl_3$). Signal multiplicities are given as singlet (s), doublet (d), triplet (t), and multiplet (m).

	[(D-bordt)$_2$Ni]	Camphorquinone	Camphor[a]
H^8/C^8	0.67 (s)/20.22[b]	0.85 (s)/20.9[b]	0.84 (s)
H^9/C^9	0.97 (s)/20.28[b]	0.99 (s)/17.2[b]	0.95 (s)
H^{10}/C^{10}	1.42 (s)/11.5	1.02 (s)/8.6	0.88 (s)
H^4/C^4	3.1 (d)/59.7	2.56 (d)/57.8	2.06 (t)
H^{5x}/C^5	2.12–2.03 (m)/25.9	2.15–2.05 (m)/22.1	1.93 (m)
H^{5n}/C^5	1.30–1.24 (m)[c]/25.9	1.59–1.52 (m)[c]/22.1	1.34 (m)
H^{6x}/C^6	1.88–1.80 (m)/32.9	1.91–1.79 (m)/29.7	1.62 (m)
H^{6n}/C^6	1.30–1.24 (m)[c]/32.9	1.59–1.52 (m)[c]/29.7	1.39 (m)

[a] From ref.[37] [b] Assignments may be reversed. [c] Overlap.

Electronic Properties: A Highly Electron-Rich Dithiolene

The redox properties of the four complexes were evaluated by cyclic voltammetry (Table 2). The nickel complexes are characterized by two reversible redox waves attributable to the –2/–1 and –1/0 redox processes together with an irreversible wave at higher potentials attributed to the 0/+1 redox process. On the other hand, only two reversible waves could be observed for the gold complexes, corresponding to the –1/0 and 0/+1 redox processes. In both nickel and gold complexes, the redox waves are strongly shifted toward more cathodic potentials when compared with literature data for other alkyl or aryl-substituted dithiolene complexes, indicating that the bornylenedithiolato ligand is probably one of the most electron-rich dithiolate ligand described so far.

Table 2. Redox potentials of the complexes and reference compounds (in V vs. SCE).

Complex	$E^{1/2}$ (–2/–1)	$E^{1/2}$ (–1/0)	$E^{1/2}$ (0/+1)	Ref.
[(DL-bordt)$_2$Ni]	–1.20	–0.43	+1.0[a]	this work
[(D-bordt)$_2$Ni]	–1.16	–0.41	+0.91	this work
[Ni(edo)$_2$]	–0.99[b]	–0.30[b]	+0.67[c]	[40]
[Ni(Et$_2$timdt)$_2$]	–0.56	–0.11	+0.78	[41]
[Ni($S_2C_2Me_2$)$_2$]	–1.16	–0.15	–	[42]
[Ni($S_2C_2Ph_2$)$_2$]	–0.87	–0.045	–	[43]
[(DL-bordt)$_2$Au]	–	–0.06	+0.62	this work
[(D-bordt)$_2$Au]	–	–0.05	+0.61	this work
[Au{S_2C_2(*p*-RO-Ph)$_2$}][d]	–	+0.24	+0.76	[28]
[Au{S_2C_2(*p*-*t*BuPh)$_2$}$_2$]	–1.70	+0.28	+0.84	[27]
[Au(dddt)$_2$]	–1.32	+0.41	+0.82[e]	[44]

[a] E_{ox} value as the process is not fully reversible. [b] Original values given vs. Ag/Ag^+ have been converted to values vs. SCE by adding 0.56 V. [c] Original values given vs. Ag/AgCl have been converted to values vs. SCE by adding –0.045. [d] R = *n*-$C_{12}H_{25}$. [e] Coupled to electrode absorption.

UV/Vis/NIR absorption spectra of the nickel and gold complexes exhibit a strong NIR absorption, characteristic of such complexes (Table 3). Note that this absorption is observed in the nickel complexes at a longer wavelength than in aryl-substituted complexes, indicating that the latter possess a smaller HOMO–LUMO gap, probably due to an increased delocalization on the aryl moieties. This effect is

not as pronounced in the radical gold complexes, in which the NIR absorption differs only slightly from one complex to the other.

Table 3. NIR absorption band characteristics of the neutral bornylenedithiolato complexes and reference compounds.

	λ /nm	ε /mol^{-1} cm^{-1}	Ref.
[(DL-bordt)$_2$Ni]	789	25 870	this work
[(D-bordt)$_2$Ni]	791	27 530	this work
[Ni($S_2C_2Me_2$)$_2$]	771	21 500	[42,45]
[Ni($S_2C_2Ph_2$)$_2$]	855	29 800	[46]
[Ni{S_2C_2(*p*-RO-Ph)$_2$}]	933	31 300	[28]
[(DL-bordt)$_2$Au]	1490	16 100	this work
[(D-bordt)$_2$Au]	1492	18 460	this work
[Au{S_2C_2(*p*-ROPh)$_2$}][a]	1566	33 400	[28]
[Au{S_2C_2(*p*-*t*BuPh)$_2$}]	1495	21 200	[27]
[Au(*t*Bu$_2$bdt)$_2$]	1452	27 000	[47]

[a] R = *n*-$C_{12}H_{25}$.

The paramagnetic nature of the two neutral gold complexes was confirmed by solution EPR spectroscopy. Both the diastereomeric mixture [(DL-bordt)$_2$Au] and the enantiopure complex [(D-bordt)$_2$Au] exhibit the same single Lorentzian resonance line with a peak-to-peak linewidth of 25 G and unresolved hyperfine coupling. The simulation gave g = 2.01(1) and A(iso) ≈ 5.8 10^{-4} cm^{-1}. Frozen solution spectra are characteristic of a rhombic system with g_{min} = 1.963, g_{int} = 2.017, g_{max} = 2.052 and $<g>$ = 2.0107. The g tensor principal values are comparable to those reported for other soluble radical gold complexes such as [Au{S_2C_2(*p*-*t*BuPh)$_2$}][27] or [Au{S_2C_2(*p*-ROPh)$_2$}].[28] In these two latter compounds, the anisotropy of the g tensor, represented by the (g_{max} – g_{min}) value, was found to decrease from 0.121 in [Au{S_2C_2(*p*-*t*BuPh)$_2$}] to 0.108 in [Au{S_2C_2(*p*-ROPh)$_2$}], a difference attributed then to the higher electron releasing ability of the alkoxy groups in [Au{S_2C_2(*p*-ROPh)$_2$}].[28] We found here for [(DL-bordt)$_2$Au] and [(D-bordt)$_2$Au] an even smaller (g_{max} – g_{min}) value (0.089), indicating the strong contribution of the two dithiolate ligands to the SOMO and confirming the strongly electron-rich character of the bornylenedithiolato ligands.

Structural Properties in the Solid State and Associated Magnetic Behavior

The X-ray crystal structures of the four complexes could be successfully resolved. The diastereomeric mixtures of the nickel [(DL-bordt)$_2$Ni] and gold [(DL-bordt)$_2$Au] complexes are isomorphous and crystallize in the monoclinic system, space group $P2_1/c$, with a molecule disordered on an inversion center (Figure 2). Indeed, despite the fact that the diastereomeric mixture contains three different isomers, that is, the two enantiomers [(D-bordt)$_2$M] and [(L-bordt)$_2$M] and the *meso* [(D-bordt)(L-bordt)M] form (M = Ni, Au), the D- and L-enantiomers of the DL-bornylenedithiolato ligand are disordered on very close positions, with a refined occupation ratio of 0.33:0.67 (Figure 2) for the nickel complexes and 0.74:0.26 for the gold complex. Furthermore, the complexes adopt a *chair* conformation, as shown in Scheme 6, in contrast to the other possible *boat* conformation.

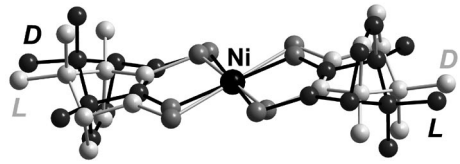
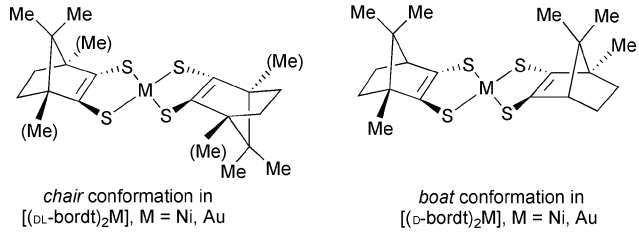


Figure 2. View of [(DL-bordt)$_2$Ni] showing the disorder of the two D and L enantiomers of the DL-bornylenedithiolato ligand. Black carbon atoms and bonds correspond to the smaller occupation parameter (0.33), light gray carbon atoms and bonds correspond to the larger occupation parameter (0.67).



Scheme 6. Solid state *chair* or *boat* conformations of complexes [(DL-bordt)$_2$M] or [(D-bordt)$_2$M], respectively.

The solid state organization of the gold complex is also particularly worth attention, as the complexes are paramagnetic. Furthermore, the spin density in such alkyl-substituted complexes is essentially localized on the metallacycles, and intermolecular interactions can be anticipated only if short intermolecular Au···Au, Au···S, or S···S contacts are observed. As shown in Figure 3, the complexes are fully isolated from each other in the *bc* plane. A view of the molecules piling up along *a* (Figure 4) shows several short lateral S···S intermolecular contacts.

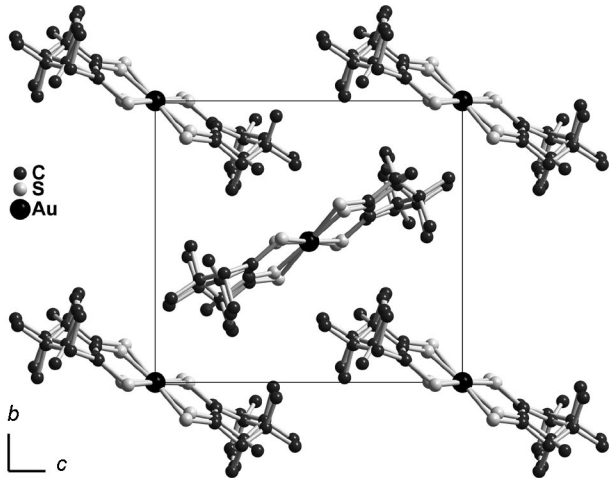


Figure 3. Projection along the *a* axis of the unit cell of the paramagnetic [(DL-bordt)$_2$Au], showing the absence of any short S···S or Au···S intermolecular contacts between the molecules in the *bc* plane.

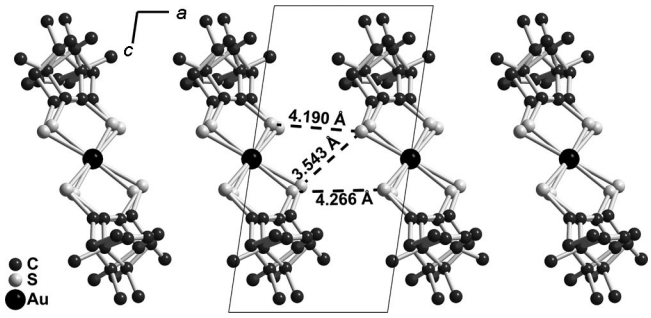


Figure 4. A view of the chains running along *a* in the structure of [(DL-bordt)$_2$Au].

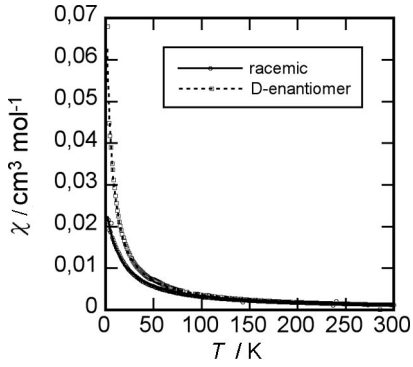


Figure 7. Temperature dependence of the magnetic susceptibility for the diastereomeric [(DL-bordt)$_2$Au] and enantiopure [(D-bordt)$_2$Au] complexes. Solid lines are fits to the Curie–Weiss law (see text).

The enantiopure complexes with nickel and gold, that is, [(D-bordt)$_2$Ni] and [(D-bordt)$_2$Au], are also isomorphous. They both crystallize in the monoclinic system, but now in the chiral space group $P2_1$. The complexes are not affected by disorder anymore but adopt a *boat* conformation (Figure 5), in contrast to the *chair* conformation found in the diastereomeric mixture. As a consequence, the solid-state organization of the two types of complexes is different. The enantiopure complexes also organize into columns running along *a*, isolated from each other in the *bc* plane by the bulky bornane moieties, but a view of these chains running along *a* (Figure 6) shows differences with the structure of the diastereomeric mixture, as only one single intermolecular lateral S···S contact at 3.45 Å is now identified.

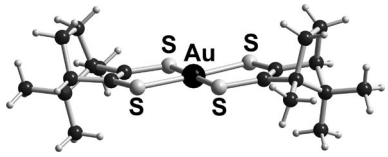


Figure 5. View of enantiopure [(D-bordt)$_2$Au]$^{\cdot}$.

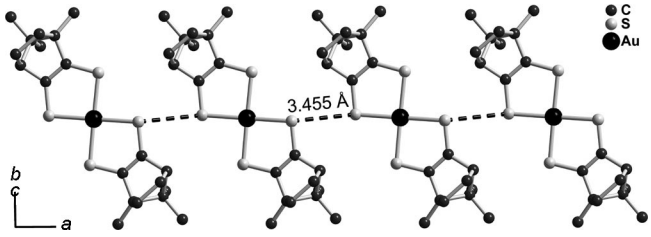


Figure 6. View of the chains of the radical enantiopure [(D-bordt)$_2$Au]$^{\cdot}$ molecules running along *a* with single short S···S intermolecular contacts.

The temperature dependence of the magnetic susceptibility for both the diastereomeric [(DL-bordt)$_2$Au] mixture and the enantiopure [(D-bordt)$_2$Au] complex is shown in Figure 7.

Despite the presence of uniform spin chains deduced from the analysis of both X-ray crystal structures, the magnetic susceptibility could not be properly fitted with the corresponding Bonner–Fischer model but with a Curie–Weiss law. The Curie–Weiss temperatures and *g* values were determined from the fit of the experimental data with $\chi = \chi_0 + Ng^2\beta^2/k(T - \theta)$, affording for the diastereomeric [(DL-bordt)$_2$Au] mixture $\chi_{dl}{}^0 \approx 0\ cm^3\,mol^{-1}$, $g_{dl} = 1.998(1)$, $\theta_{dl} = -14.7(2)$ K, and for [(D-bordt)$_2$Au], $\chi_d{}^0 = 1.3(1) \times 10^{-4}\ cm^3\,mol^{-1}$, $g_d = 1.998(1)$, $\theta_d = -4.0(1)$ K. The stronger antiferromagnetic interactions [$\theta_{dl} = -14.7(2)$ K vs. $\theta_d = -4.0(1)$ K] found for the diastereomeric complex are most probably correlated with the different overlap interaction patterns between molecules along the *a* direction, as detailed above in Figure 4 and Figure 6.

Conclusions and Perspectives

In this paper we have described novel paramagnetic gold dithiolene complexes characterized by a chiral functionality. An efficient synthesis of bornylenedithiolene complexes derived has been established, based on the reaction of camphorquinone with P_4S_{10} in dimethylimidazolidinone followed by addition of the gold salt $KAuCl_4$. The known complexity of the ^{1}H NMR signal assignments of camphor derivatives has been addressed here for the diamagnetic nickel complexes by a combination of 2D NMR spectroscopy experiments. Electrochemical and EPR properties demonstrate that the bornylenedithiolato ligand acts as a highly electron-rich dithiolato ligand. Its strongly dissymmetrical shape allows for two different (*boat* or *chair*) conformations in the solid state: the centrosymmetric *chair* conformation was observed in the X-ray crystal structure of the diastereomeric [(DL-bordt)$_2$Au] mixture, with the two enantiomeric dithiolene ligands disordered on the same inversion centered site. The differences between the X-ray crystal structures of the two gold complexes lead to different interaction paths through lateral S···S intermolecular interactions, at the origin of the stronger antiferromagnetic Curie–Weiss temperature in the diastereomeric mixture. The avail-

ability of these soluble complexes offers several attractive perspectives. For example, the electron-rich character of the nickel complexes lets us infer that they might be oxidized themselves as cation radical salts, as reported for example for the [Ni(dddt)$_2$] complexes.[48]

Experimental Section

Procedures and Methods: ^{1}H and ^{13}C NMR spectra were recorded with Bruker 300 and 500 MHz instruments (^{1}H NMR spectra were recorded at 300 and 500 MHz, and ^{13}C NMR spectra were recorded at 75 and 125 MHz); chemical shifts are reported in ppm and J values in Hz. In the ^{13}C NMR spectra, signals corresponding to CH, CH$_2$, or Me groups, assigned from DEPT, are noted; all others are C. The residual signals for the NMR spectroscopic solvents are: for $CDCl_3$, 7.26 ppm for the proton and 77.00 ppm for the carbon. The following abbreviations have been used for the assignments: s for singlet, d for doublet, t for triplet, q for quintet, and m for multiplet. UV/Vis/NIR spectra were recorded with a Cary 5 spectrophotometer in CH_2Cl_2. Cyclic voltammetry was carried out on a 1.5×10^{-3} M solution of metal complex in CH_2Cl_2 (anhydrous grade) containing nBu$_4$NPF$_6$ (0.2 M) as supporting electrolyte. Voltammograms were recorded at 0.1 V s^{-1} on a platinum disk electrode (1 mm^2). Potentials were measured vs. the saturated calomel electrode (SCE). Elemental analyses were performed at the CNRS Service de Microanalyse, Gif sur Yvette, France. Optical rotation of the enantiopure compounds was determined with a Perkin–Elmer 341 polarimeter. EPR data were collected with a Bruker ELEXSYS 500 spectrometer.

Synthesis of the Nickel Complexes: A mixture of (DL)-camphorquinone or D-camphorquinone (1 g, 6 mmol) and P_4S_{10} (5.34 g, 12 mmol) in 1,3-dimethyl-2-imidazolidinone (50 mL) was maintained at 110 °C for 2 h. The reaction mixture was cooled to 60 °C. A solution of nickel chloride hexahydrate (0.72 g, 3 mmol) in water (5 mL) was added, and the reaction mixture was warmed to 90 °C for 2 h in air. After cooling to room temperature, EtOH (100 mL) was added, and the precipitate was filtered, washed with EtOH, and dried under vacuum. The dark purple solid was recrystallized by slow diffusion of MeOH into a CH_2Cl_2 solution of the product.

[(DL-bordt)$_2$Ni]: Dark purple crystals; 1.01 g, 74% yield; m.p. 277 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.67 (s, 6 H, CH$_3$), 0.97 (s, 6 H, CH$_3$), 1.22–1.31 (m, 4 H, H^{5n}/H^{6n}), 1.41 (s, 6 H, CH$_3$), 1.77–1.90 (m, 2 H, H^{6x}), 2.00–2.15 (m, 2 H, H^{5x}), 3.09 (d, J = 4.1 Hz, 2 H, H^4) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 11.49 (Me), 20.20 (Me), 20.25(Me), 25.91 (CH$_2$), 32.85 (CH$_2$), 59.62 (CH), 61.41 (C), 61.94 (C), 193.72 (C), 198.49 (C) ppm. $C_{20}H_{28}NiS_4$ (455.37): calcd. C 52.75, H 6.20; found C 52.63, H 6.31. UV/Vis/NIR (CH_2Cl_2): λ_{max} (ε, M^{-1} cm^{-1}) = 305 (47000), 396 (920), 547 (420), 789 (25 870) nm.

[(D-bordt)$_2$Ni]: Dark purple crystals; 1.05 g, 77% yield; m.p. 279 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.67 (s, 6 H, CH$_3$), 0.97 (s, 6 H, CH$_3$), 1.24–1.30 (m, 4 H, H^{5n}/H^{6n}), 1.42 (s, 6 H, CH$_3$), 1.80–1.88 (m, 2 H, H^{6x}), 2.03–2.12 (m, 2 H, H^{5x}), 3.1 (d, J = 4.1 Hz, 2 H, H^4) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 11.5 (Me), 20.22 (Me), 20.28 (Me), 25.9 (CH$_2$), 32.9 (CH$_2$), 59.7 (CH), 61.4 (C), 61.9 (C), 193.7 (C), 198.5 (C) ppm. $C_{20}H_{28}NiS_4$ (455.37): calcd. C 52.75, H 6.20; found C 52.78, H 6.25. UV/Vis/NIR (CH_2Cl_2): λ_{max} (ε, M^{-1} cm^{-1}) = 305 (41000), 396 (1130), 547 (670), 791 (27 530) nm. $[a]_D^{20}$ = –280 (2×10^{-4} M, CH_2Cl_2).

Gold Complexes

[(DL-bordt)$_2$Au]: A mixture of (DL)-camphorquinone (220 mg, 1.3 mmol) and P_4S_{10} (1.18 g, 2.6 mmol) in 1,3-dimethyl-2-imidazolidinone (10 mL) was maintained at 110 °C for 2 h. The reaction mixture was cooled to 60 °C. A solution of potassium tetrachloroaurate(III) (0.227 g, 0.6 mmol) in water (5 mL) was added, and the reaction mixture was warmed to 90 °C for 2 h in air. After cooling to room temperature, EtOH (25 mL) was added, and the precipitate was filtered, washed with EtOH, and dried under vacuum. The purification of products was carried out by chromatography on silica gel, eluting with petroleum ether/CH_2Cl_2 (7:3). The

Table 4. Crystallographic data.

Phase	[(DL-bordt)$_2$Ni]	[(DL-bordt)$_2$Au]	[(D-bordt)$_2$Ni]	[(D-bordt)$_2$Au]
Formula	$C_{20}H_{28}NiS_4$	$C_{20}H_{28}AuS_4$	$C_{20}H_{28}NiS_4$	$C_{20}H_{28}AuS_4$
Fw	455.37	593.63	455.37	593.63
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1$	$P2_1$
a /Å	6.9304(10)	6.8824(4)	7.6762(2)	7.6982(4)
b /Å	11.986(3)	12.1179(12)	12.5926(3)	12.6140(6)
c /Å	13.252(3)	13.3817(11)	11.3231(3)	11.3296(5)
β /°	99.167(16)	98.517(6)	91.290(2)	91.296(2)
V /Å^3	1086.7(4)	1103.73(16)	1094.25(5)	1099.88(9)
Z	2	2	2	2
d_{calc} /Mg m^{-3}	1.392	1.786	1.382	1.792
temp /K	293(2)	293(2)	293(2)	100(2)
μ /mm^{-1}	1.278	7.044	1.269	1.792
θ-range /°	3.55–27.5	3.51–27.5	2.65, 32.05	1.80, 27.53
Measured reflections	19516	32060	14948	23356
Independent reflections	2480	2527	7301	4937
R_{int}	0.0407	0.0343	0.0449	0.0342
$I > 2\sigma(I)$ reflections	2029	2317	5897	4845
Absorption correction	multiscan	multiscan	multiscan	multiscan
T_{min}, T_{max}	0.783, 1.0	0.715, 0.970	0.6227, 0.8763	0.090, 0.243
Refined parameters	224	184	227	232
$R(F), I > 2\sigma(I)$	0.0377	0.055	0.0395	0.0227
$wR(F^2)$, all	0.0906	0.1192	0.1139	0.0510
Flack's parameter	–	–	–0.005(10)	0.049(6)
$\Delta\rho$ /e Å^{-3}	0.278, –0.258	0.712, –1.794	0.062, –0.495,	2.280, –1.550

dark purple solid was recrystallized by slow evaporation of the solvent from a Et_2O solution to afford the title compound as dark purple crystals, 0.15 g, 38% yield; m.p. 229 °C. $C_{20}H_{28}AuS_4$ (593.63): calcd. C 40.46, H 4.75; found C 40.48, H 4.67. UV/Vis/NIR (CH_2Cl_2): λ_{max} (ε, $M^{-1}cm^{-1}$) = 516 (1740), 1490 (16 100) nm.

[(D-bordt)$_2$Au]: A mixture of D-camphorquinone (1 g, 6 mmol) and P_4S_{10} (5.34 g, 12 mmol) in 1,3-dimethyl-2-imidazolidinone (50 mL) was maintained at 110 °C for 2 h. The reaction mixture was cooled to 60 °C. A solution of potassium tetrachloroaurate(III) (1.23 g, 3 mmol) in water (5 mL) was added, and the reaction mixture was warmed to 90 °C for 2 h in air. After cooling to room temperature, EtOH (100 mL) was added, and the precipitate was filtered, washed with EtOH, and dried under vacuum. The purification of products was carried out by chromatography on silica gel, eluting with petroleum ether/CH_2Cl_2 (7:3). The dark purple solid was recrystallized by slow evaporation of the solvent from a Et_2O solution to afford the title compound as dark purple crystals, 0.42 g, 24% yield; m.p. 231 °C. $C_{20}H_{28}AuS_4$ (593.65): calcd. C 40.46, H 4.7; found C 40.57, H 4.89. UV/Vis/NIR (CH_2Cl_2): λ_{max} (ε, $M^{-1}cm^{-1}$) = 516 (1540), 1492 (18 460) nm. $[\alpha]_D^{20} = -150$ (4×10^{-4} M, CH_2Cl_2).

Crystallography: Experimental data and refinement results are given in Table 4. Data were collected with an APEX II Bruker AXS diffractometer with Mo-K_α radiation (λ = 0.71073 Å). Structures were solved by direct methods (SHELXS97[49] or SIR92)[50] and refined (SHELXL-97)[49] by full-matrix least-squares methods as implemented in the WinGX software package.[51] An empirical absorption (multi-scan) correction was applied. Hydrogen atoms were introduced at calculated positions (riding model) included in the structure factor calculation but not refined. CCDC-746500, -746501, -746502, -746503 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.

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