# Redox Chemistry

# Correlated Coordination and Redox Activity of a Hemilabile Noninnocent Ligand in Nickel Complexes

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**Abstract:** The compound  $[Ni(Q_M)_2]$ ,  $Q_M = 4,6$ -di-*tert*-butyl-*N*-(2-methylthiomethylphenyl)-*o*-iminobenzoquinone, is a singlet diradical species with approximately planar configuration at the tetracoordinate metal atom and without any Ni–S bonding interaction. One-electron oxidation results in additional twofold Ni–S coordination ( $d_{Ni-S} \approx 2.38$  Å) to produce a complex cation of  $[Ni(Q_M)_2](PF_6)$  with hexacoordinate Ni<sup>II</sup> and two distinctly different *mer*-configurated tridentate ligands. The O,O'-*trans* arrangement in the neutral precursor is changed to an O,O'-*cis* configuration in the cation. The EPR signal of  $[Ni(Q_M)_2](PF_6)$  has a very large *g* anisotropy and the magnetic measurements indicate an  $S = \frac{3}{2}$  state. The dication was structurally characterized as  $[Ni(Q_M)_2](CIO_4)_2$  to exhibit a similar NiN<sub>2</sub>O<sub>2</sub>S<sub>2</sub> framework as the monocation. However, the two tridentate (O,N,S) ligands are now equivalent

according to the formulation  $[Ni^{II}(Q_M^{0})_2]^{2+}$ . Cyclic voltammetry reflects the qualitative structure change on the first, but not on the second oxidation of  $[Ni(Q_M)_2]$ , and spectroelectrochemistry reveals a pronounced dependence of the 800–900 nm absorption on the solvent and counterion. Reduction of the neutral form occurs in an electrochemically reversible step to yield an anion with an intense near-infrared absorption at 1345 nm ( $\varepsilon = 10400 \text{ m}^{-1} \text{ cm}^{-1}$ ) and a conventional *g* factor splitting for a largely metal-based spin ( $S = \frac{1}{2}$ ), suggesting a  $[(Q_M^{-})Ni^{II}(Q_M^{2-})]^{-}$  configuration with a tetracoordinate metal atom with antiferromagnetic Ni<sup>II</sup>–(Q<sub>M</sub><sup>--</sup>) interactions and symmetry-allowed ligand-to-ligand intervalence charge transfer (LLIVCT). Calculations are used to understand the Ni–S binding activity as induced by remote electron transfer at the iminobenzoquinone redox system.

# Introduction

Hemilabile ligands<sup>[1]</sup> are increasingly acknowledged as valuable components of functional coordination compounds.<sup>[2]</sup> The control of hemilability beyond equilibria situations is an attractive goal, for example, in catalysis.<sup>[1,2]</sup> One parameter to control hemilability is the redox state of the metal, which may prefer larger or smaller coordination numbers. The copper(II/I) redox pair is a prominent case in point.<sup>[3]</sup> However, the hemilabile ligand itself can also be redox active, leading to potentially noninnocent behavior<sup>[4]</sup> in transition metal complexes. In connection with the H<sub>2</sub>-activation research described by Ringenberg, Rauchfuss et al.,<sup>[5]</sup> we have thus described a redox-active iminobenzoquinone ligand with an additional thioether donor function,  $Q_y = 4,6$ -di-*tert*-butyl-*N*-(2-methylthiophenyl)-o-iminobenzoquinone, where the S-donor atom coordinates to

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Scheme 1. Intramolecular oxidative addition involving a hemilabile noninnocent ligand  $\mathbf{Q}_{\mathbf{y}}$ 

 $[Ir(C_5Me_5)]^{2+}$  in the semiquinone state, but not in the fully reduced amidophenolate form (Scheme 1).  $^{[6]}$ 

On the other hand, the three-spin complex  $[(Q_y^{-})Cu^{II}(Q_y^{-})]$  showed a single weak metal–S coordination accompanied by twisting of the CuN<sub>2</sub>O<sub>2</sub> core and ligand-based spin<sup>[7]</sup> in contrast to the planar parent system  $[(Q^{-})Cu^{II}(Q^{-})]$  without S-donor function (Scheme 2).<sup>[8]</sup>



Scheme 2. Twisting and S coordination in copper(II) complexes of *o*-iminobenzosemiquinones (ref. [7]).

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One of the most striking examples in the popular<sup>[5-11]</sup> coordination chemistry that involves redox-active amidophenolate/ iminobenzoquinone ligands, is the planar configuration at the nickel atom, analyzed experimentally and theoretically as [(Q<sup>--</sup>)Ni<sup>II</sup>(Q<sup>--</sup>)].<sup>[8,9]</sup> Similar to the *o*-diiminobenzosemiquinonato analogues,<sup>[12-14]</sup> the diamagnetic compounds were addressed as "singlet diradicals"<sup>[13-15]</sup> due to the antiferromagnetic coupling of the structurally identified iminosemiquinone ligands through the low-spin nickel center.<sup>[9]</sup> Metric parameters are usually accepted as valid indicators for the oxidation state of these Q ligands.<sup>[8,9,13,16]</sup> Redox reactions have shown that the cations of the all-N donor systems are accessible,<sup>[13a]</sup> whereas apparent two-electron oxidation processes of the iminosemiquinonato complexes lead to dications.<sup>[8,10b,17,18]</sup> The structures of  $[(Q_v^{\bullet})Ni^{II}(Q_v^{\bullet})]^{[17]}$  and related species<sup>[18]</sup> show a similar planar NiN<sub>2</sub>O<sub>2</sub> configuration as in  $[(Q^{-})Ni^{\parallel}(Q^{-})]$ ,  $Q^{-} = 4,6$ -ditert-butyl-N-phenyl-o-iminobenzosemiquinone,<sup>[8]</sup> without Ni-S bonding.

The particular electrochemical oxidation behavior during cyclic voltammetry experiments<sup>[17]</sup> of  $[(Q_y^{-})Ni^{ll}(Q_y^{-})]$  has prompted us to investigate this process in detail, employing the more flexible, tridentate, new, (O,N,S) ligand  $Q_M = 4,6$ -di*tert*-butyl-*N*-(2-methylthiomethylphenyl)-*o*-iminobenzoquinone. Spectroelectrochemical (UV-visible-NIR, EPR) and structural information could now be collected for the redox series  $[Ni(Q_M)_2]^{0/+/2+}$ ,  $1^{0/+/2+}$ , whereas the anion was studied with spectroelectrochemistry. The purpose was to establish the appropriate oxidation-state combinations for each state on the basis of experimental and DFT-calculated spectroscopic and structural changes.



Nickel complexes [NiL<sub>2</sub>]<sup>*n*</sup> with noninnocent, quinonoid, chelate ligands L have attracted attention for several decades<sup>[8-14]</sup> because of the multiple redox activity/processes, the puzzling structures, and oxidation-state situations. Whereas the electronic structures have been discussed in detail by Wieghardt, Neese, and co-workers, the ionic species have only been partially characterized: Anions were obtained as intermediates of two one-electron steps, whereas the oxidations showed a less well-defined response, partially appearing as irreversible twoelectron processes.<sup>[8, 10b, 13, 14, 17, 18]</sup> Our present contribution will shed light on the changes that occur during oxidation of compound **1** and thus provide further insight into the bonding potential of hemilabile noninnocent ligands.

# **Results and Discussion**

### Synthesis, structure and spectroscopy of 1

The new, hemilabile, noninnocent ligand  $Q_M$  was obtained in the conventional way.<sup>[7,8,11]</sup> The reaction with NiCl<sub>2</sub> yields complex **1**, identified by elemental analysis, mass spectroscopy, <sup>1</sup>H NMR spectroscopy (see the Experimental Section) and by two crystal structures, one of a solvent-free form (Tables 1, 2, and S3 in the Supporting Information, Figure 1) and one of an acetonitrile solvate (Tables S1,S2 and Figure S1 in the Support-



Figure 1. Molecular structure of 1 in the crystal.

ing Information). Both structures show an approximately planar NiO<sub>2</sub>N<sub>2</sub> configuration with the thioether sulfur atoms at nonbonding distances (5.507(1) and 5.767(1) Å for **1**, 5.066(1) and 3.712(1) Å for **1**×0.3 CH<sub>3</sub>CN). The configuration at the metal atom reveals slight deviation from planarity (Table S4 in the Supporting Information). In spite of this slight distortion, which has also been observed for the corresponding neutral complexes [(L<sup>-</sup>)Ni(L<sup>-</sup>)],<sup>[8,9]</sup> the potentially O,N,S tridentate ligands coordinate only in a bidentate fashion with *trans*-positioned O and N donors. The results are reproduced by DFT calculations (Table 2). In agreement with earlier reports<sup>[8-14]</sup> on similar species, complex **1** displays a very intense absorption with a  $\lambda_{max}$  value at 894 nm ( $\varepsilon = 26000 \text{ m}^{-1} \text{ cm}^{-1}$ ).

The <sup>1</sup>H NMR spectrum of **1** in  $[D_8]$ toluene is influenced by dynamic effects, which involve the flexible, saturated, – CH<sub>2</sub>SCH<sub>3</sub> side arms,<sup>[19]</sup> and by marginal paramagnetism (see below). Temperature-dependent measurements (Figure S2 in the Supporting Information) show the expected, slightly broadened signals in the unsymmetrically frozen configuration at 223 K (see the Experimental Section) and broadening, shifting, and partially coalescing signals at higher temperatures, until 348 K. Superconducting quantum interference device (SQUID) susceptibility and EPR measurements of **1** (powder) at variable temperatures showed only very weak paramagnetic response, in agreement with the largely planar configuration around the metal atom.

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Table 1. Crystallographic data.				
	1 <sup>[a]</sup>	$[1](PF_6) \times CH_2CI_2$	[1](ClO <sub>4</sub> ) <sub>2</sub> ×0.25CH <sub>2</sub> Cl <sub>2</sub>	
formula	C <sub>44</sub> H <sub>58</sub> N <sub>2</sub> NiO <sub>2</sub> S <sub>2</sub>	$C_{45}H_{60}CI_2F_6N_2NiO_2PS_2$	C <sub>44.25</sub> H <sub>58.5</sub> Cl <sub>2.5</sub> N <sub>2</sub> NiO <sub>10</sub> S <sub>2</sub>	
<i>M</i> <sub>r</sub>	/69./5	999.65	989.90	
crystal system	monoclinic	triclinic	monoclinic	
space group	$P2_1/n$	<i>P</i> 1	C2/c	
cell dimensions [A,°]	a = 18.277(1)	a = 11.028(1)	a = 79.521(4)	
	b = 10.1072(6)	b = 15.140(1)	b = 13.5097(7)	
	c = 23.657(1)	c=15.299(1)	c=20.7353(9)	
	$\alpha = 90$	$\alpha = 100.215(4)$	$\alpha = 90$	
	$\beta =$ 105.044(4)	$\beta =$ 93.383(4)	$\beta = 103.894(2)$	
	$\gamma = 90$	$\gamma = 95.550(4)$	$\gamma = 90$	
V [Å <sup>3</sup> ]	4220.3(4)	2494.5(4)	21624(2)	
crystal size [mm]	0.14; 0.07; 0.02	0.25; 0.15; 0.04	0.12; 0.07; 0.06	
Ζ	4	2	2	
<i>Т</i> [K]	100(2)	100(2)	100	
λ [Å]	1.54178	0.71073	1.54178	
$\theta$ range	2.74–66.52°	1.37–28.62°	2.29–66.62°	
index range	$-20 \le h \le 21$	$-14 \le h \le 14$	$-93 \le h \le 87$	
-	$-11 \le k \le 12$	$-20 \le k \le 20$	$-15 \le k \le 15$	
	$-27 \le l \le 27$	$-20 \le l \le 20$	$-17 \le l \le 24$	
refins collected	24888	90974	119471	
independent reflns	7197	12621	18246	
data/restraints/parame-	7197/0/460	12621/0/564	18246/0/1163	
ters				
goodness-of-fit	1.019	1.026	1.035	
R(int)	0.0734	0.0442	0.0619	
$R_1[l > 2\sigma(l)]$	0.0616	0.0442	0.0572	
$R_1$ (all data)	0.0990	0.0619	0.0710	
wR ( $F^2$ ) [ $F^2 > 2\sigma(F^2)$ ]	0.1555	0.1046	0.1587	
wR (F <sup>2</sup> ) (all data)	0.1783	0.1119	0.1695	
$\Delta ho_{max};\Delta ho_{min}$ [e Å <sup>-3</sup> ]	1.490; -0.783	3.293; -1.084	1.735; -0.606	
[a] Crystals from CH <sub>2</sub> Cl <sub>2</sub> /CH <sub>3</sub> OH solution. The structure of an acetonitrile solvate with				

slightly better crystal quality is given in Tables S1–S3 and Figure S1 in the Supporting Information.

### Electrochemistry and structures of oxidized forms

Compound 1 exhibits two reduction and two oxidation waves in cyclic voltammetry experiments, shown for ambient and low-temperature situations (see Figure 2) and Table 3). The first reduction is completely reversible, whereas the second reduction process is not fully reversible, as confirmed by UV-visible-NIR spectroelectrochemistry. The one-electron oxidation wave in the cyclic voltammogram (Figure 2) is considerably distorted; this reflects the structurally



Figure 2. Cyclic voltammograms of 1 in  $CH_2CI_2/Bu_4NPF_6$  (0.1 M) at 298 and 233 K (100 mV s<sup>-1</sup> scan rate).

established coordination change. On the other hand, once generated, the cation  $1^+$  exhibits a reversible oxidation to  $1^{2+}$ .

The electrochemical (and spectroelectrochemical) results can be understood from the molecular structures (Tables 1, 2, and S3 in the Supporting Information, Figure 3, Figure 4). Compound 1 could be oxidized chemically to [1](PF<sub>6</sub>) and [1](ClO<sub>4</sub>)<sub>2</sub> by silver salts. Both ions  $1^+$  and  $1^{2+}$  show hexacoordination in the crystal with two normal Ni-S bond lengths of about 2.38 Å and with changed configuration, that is, cis-positioned O donors at the nickel atom in contrast to trans-positioned O centers in nonoxidized 1. This configuration, which results from the necessity to have two mer-coordinating tridentate ligands at the central metal ion, must involve an intermediate bond dissociation and rearrangement (Scheme 3). At low temperature a single two-electron oxidation peak is observed (Figure 2); this suggests that the prevailing oxidation mechanism under these conditions includes two close one-electron transfers, followed by a rearrangement in the coordination sphere, that is, an EEC process different from the EC+E mechanism observed at room temperature.

Inspection of [1](PF<sub>6</sub>) and [1](ClO<sub>4</sub>)<sub>2</sub> shows that the monocation 1<sup>+</sup> contains two distinctly different ligands, assigned as  $Q_M^{\bullet-}$  and  $Q_M^{\bullet0}$  on the basis of the well-established<sup>[8,9,14,16]</sup> metrical parameters C–O, C–N and C–C within the quinonoid ring. The dicationic 1<sup>2+</sup> contains two very similar ligands, identified as  $Q_M^{\bullet0}$ .

The DFT-optimized geometry of the neutral complex 1 reproduces the experimental crystal structures



Scheme 3. Conversion of complexes 1<sup>n</sup> on electron transfer.



Figure 3. Molecular structure of  $1^+$  in the crystal of  $[1](PF_6) \times CH_2CI_2$ .

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			Selected distance	es [Å]			
	1 <sup>(b</sup>	]	[1]+		[ <b>1</b> ] <sup>2</sup>	+	[1]-
	exptl	calcd	exptl	calcd	exptl	calcd	calcd
Ni(1)–O(1)	1.832(3)	1.817	2.112 (2)	2.089	2.087(2)	2.058	1.829
Ni(1)–O(2)	1.831(3)	1.819	2.018(2)	2.002	2.112(2)	2.058	1.833
Ni(1)–N(1)	1.835(3)	1.827	2.058(2)	2.102	2.056(3)	2.087	1.841
Ni(1)–N(2)	1.839(3)	1.825	2.013(2)	2.014	2.056(3)	2.087	1.837
Ni(1)-S(1)	5.507(1)	5.215	2.3957(6)	2.426	2.356(1)	2.405	5.063
Ni(1)–S(2)	5.767(1)	5.413	2.3778(6)	2.422	2.365(1)	2.405	5.370
O(1)-C(1)	1.315(5)	1.297	1.239(3)	1.232	1.235(4)	1.239	1.314
C(1)–C(2)	1.413(5)	1.422	1.459(3)	1.459	1.456(5)	1.452	1.412
C(2)-C(3)	1.377(6)	1.381	1.351(3)	1.356	1.350(5)	1.359	1.394
C(3)–C(4)	1.430(6)	1.423	1.465(3)	1.458	1.468(5)	1.460	1.405
C(4)-C(5)	1.371(6)	1.375	1.344(3)	1.354	1.347(5)	1.356	1.388
C(5)–C(6)	1.414(5)	1.411	1.438(3)	1.435	1.433(5)	1.432	1.402
C(6)-C(1)	1.431(5)	1.433	1.516(3)	1.511	1.514(5)	1.512	1.421
N(1)–C(6)	1.353(5)	1.348	1.299(3)	1.298	1.304(4)	1.303	1.368
O(2)-C(30)	1.322(4)	1.297	1.295(2)	1.285	1.240(4)	1.239	1.314
C(30)–C(31)	1.417(5)	1.422	1.432(3)	1.433	1.459(5)	1.452	1.412
C(31)–C(32)	1.381(5)	1.381	1.372(3)	1.376	1.343(5)	1.359	1.395
C(32)–C(33)	1.424(5)	1.424	1.430(3)	1.427	1.471(5)	1.460	1.405
C(33)-C(34)	1.368(5)	1.375	1.364(3)	1.369	1.347(5)	1.356	1.389
C(34)–C(35)	1.418(5)	1.411	1.422(3)	1.418	1.426(5)	1.432	1.402
C(35)–C(30)	1.429(5)	1.433	1.454(3)	1.456	1.512(4)	1.512	1.422
N(2)–C(35)	1.351(5)	1.348	1.353(3)	1.345	1.306(4)	1.303	1.366

tronic configurations of the oxi-
dized species were examined in
order to find the lowest energy
state. The DFT calculations show
the <sup>4</sup> A state of the octahedral
conformation of $1^+$ as the most
stable, The <sup>4</sup> A state lies 0.05 eV
lower than the <sup>2</sup> A state and
about 1 eV lower than the
planar <sup>2</sup> A configuration. The <sup>3</sup> A
state was found at the lowest
energy level of doubly oxidized
1 <sup>2+</sup> . Bonding parameters of the
lowest energy states are listed in
Table 2, indicating how the oxi-
dation and reduction influences
the structure of <b>1</b> <sup><i>n</i></sup> .

# EPR, magnetism, and UV-visible-NIR spectroelectrochemistry

The odd-electron species  $1^-$  and  $1^+$  were generated for X-band EPR spectroscopy by in situ electrolysis ( $1^-$ ) or chemical oxidation (AgClO<sub>4</sub>:  $1^+$ ). The fully re-

Process	1 (in CH <sub>2</sub> Cl <sub>2</sub> )	[1](PF <sub>6</sub> ) (in CH <sub>3</sub> CN)
<b>1</b> <sup>+</sup> ⇔ <b>1</b> <sup>2+</sup>	0.03 ( $E_{1/2}$ ) $\Delta E = 72$	$0.06 (E_{1/2})$ $\Delta E = 75$
1⇔1⁺	-0.28 ( <i>E</i> <sub>pa</sub> 1) -0.09 ( <i>E</i> <sub>pa</sub> 2) -0.38 (E <sub>pc</sub> )	-0.23 ( <i>E</i> <sub>pa</sub> ) -0.33 ( <i>E</i> <sub>pc</sub> )
1⇔1⁻	$-1.04 (E_{1/2})$ $\Delta E = 70$	$-0.88 (E_{1/2})$ $\Delta E = 64$
$1^{-} \Leftrightarrow 1^{2-}$	-1.87 (E <sub>pc</sub> ) -1.72 (E <sub>pa</sub> )	$-1.62 (E_{1/2})$ $\Delta E = 101$



Figure 4. Molecular structure of  $1^{2+}$  in the crystal of  $[1](ClO_4)_2 \times 0.25CH_2Cl_2$ .

(Tables 2, and S2 and S3 in the Supporting Information). The bond lengths of 1 are confirmed within 0.02 Å (excluding the nonbonding Ni–S distances). Several conformations and elec-

versible reduction of 1 produces an unresolved EPR signal at g = 2.041 at room temperature and an axial g factor component splitting in the frozen state at 110 K (Figure 5). The data



Figure 5. Experimental and simulated EPR spectrum of electrolytically generated  $1^-$  in CH<sub>2</sub>Cl<sub>2</sub>/Bu<sub>4</sub>NPF<sub>6</sub> (0.1 M) at 110 K.

(Table 4) suggest a predominantly organic radical, a semiquinone radical anion,<sup>[8,20]</sup> with non-negligible metal contribution, which is responsible for the *g* anisotropy due to the spin-orbit coupling contribution from nickel. Within a localized description, a  $[(Q_M^{--})Ni^{II}(Q_M^{2-})]^-$  situation can thus be postulated, with a low-spin Ni<sup>II</sup> center bound by catecholate and with the residual spin (S = 1/2) largely on one of the semiquinone ligands. The delocalized alternative with two equivalent ligands  $Q_M^{1.5-}$  is favored by DFT calculations (Table 2), however, it would also involve ligand-centered spin. Yet another formulation,  $[(Q^-)Ni^{I-}(Q^{--})]^-$ , involving three spins,<sup>[7]</sup> can be constructed; this must, however, imply one antiferromagnetically coupled semiqui-

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Table 4. EPR data for complex cation and anion.				
	[1]+	[ <b>1</b> ] <sup>-[a]</sup>		
g <sub>1</sub> (110 K)	4.88	2.104		
<i>g</i> <sub>2</sub>	3.32	2.014		
$g_3$	2.00	2.001		
A <sub>3</sub> ( <sup>14</sup> N) <sup>[b]</sup>	n.o.	1.0		
g <sub>iso</sub> (295 K)	n.o.	2.041		
[a] From in situ electrolysis of 1 in CH <sub>2</sub> Cl <sub>2</sub> /Bu <sub>4</sub> NPF <sub>6</sub> (0.1 м). <sup>[b]</sup> In mT.				

none-metal pair in order to produce the observed ligand-centered spin. Such semiquinone-d<sup>9</sup>-semiquinone arrangements have been reported for copper(II) species<sup>[7,8]</sup> with metal-based spin for the planar system<sup>[8]</sup> and ligand-centered spin for a twisted configuration (Scheme 2).<sup>[7]</sup>

The mono-oxidized form  $1^+$  is EPR-silent at ambient temperature, but displays a broad EPR signal with high *g* anisotropy at 110 K (Figure 6, Table 4). Combined with the structural evi-



Figure 6. Experimental and simulated EPR spectrum of oxidatively (AgClO<sub>4</sub>) generated  $1^+$  in CH<sub>2</sub>Cl<sub>2</sub> at 110 K.

dence for  $[(Q_M^{-})Ni^{II}(Q_M^{0})]^+$ , this result can be traced to an  $S = \frac{3}{2}$  situation (DFT: <sup>4</sup>A state) as described earlier for related semiquinonatonickel(II) and phenoxylnickel(II) species;<sup>[21]</sup> this is typical for a transition of a Kramers' doublet with an  $S = \frac{3}{2}$  ground state and zero-field splitting larger than the X-band microwave energy (ca. 0.3 cm<sup>-1</sup>). Due to the odd electron number, the ground and exited state split into Kramers' doublets, and owing to the zero-field splitting, there are only transitions possible between the doublet states. The *g*-values are attributed to an effective spin  $S' = \frac{1}{2}$ . The high-spin Ni<sup>II</sup> configuration is favored by the neutral and weak<sup>[22]</sup> *o*-iminoquinone ligand and by the hexacoordination.

The temperature dependence of the magnetic moment of  $1(\text{ClO}_4)$  is shown in Figure 7. The value of  $\mu_{\text{eff}}(300 \text{ K}) = 4.55 \,\mu_{\text{B}}$  fits well with  $\mu_{\text{eff}}$  calculated for a noninteracting  $S = (1 + \frac{1}{2})$  system with g = 2 ( $\mu_{\text{eff}}(\text{s.o.}) = 4.56 \,\mu_{\text{B}}$ ; s.o. = spin only). On lowering the temperature, the magnetic moment decreases to a value of  $\mu_{\text{eff}}(20 \text{ K}) = 3.73 \,\mu_{\text{B}}$ , that is, close to the spin-only value for  $S = \frac{3}{2}$  ( $\mu_{\text{eff}}(\text{s.o.}) = 3.88 \,\mu_{\text{B}}$ ). On further lowering of the temperature, the magnetic moment shows a pronounced decrease to  $\mu_{\text{eff}}(1.8 \text{ K}) = 2.59 \,\mu_{\text{B}}$ , attributed to zero-field splitting, which is also responsible for the inter-Kramers' doublet transition detectable by EPR. An alternative explanation would be intermolecular antiferromagnetic coupling, which, however, is



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Figure 7. Temperature dependence of the effective magnetic moment of  $[1](CIO_4)$ .

not obvious from the crystal structure of the PF<sub>6</sub> salt; the situation may change with a different anion. Intermolecular antiferromagnetic exchange may also be the reason for the increase of the effective magnetic moment with temperatures above 20 K; this should not occur with an  $S = \frac{3}{2}$  ground state resulting from intramolecular ferromagnetic coupling, as suggested by EPR and DFT calculations.

Further support for intramolecular ferromagnetic and intermolecular antiferromagnetic coupling in  $1(CIO_4)$  is provided by the low-temperature (1.8 K) magnetization curve (Figure 8).



Figure 8. Field dependence of the magnetization of [1](ClO<sub>4</sub>).

Compound 1(ClO<sub>4</sub>) has a magnetization value of 2.63  $\mu_B$  at 7 T, which is much higher than expected for an  $S = \frac{1}{2}$  system, but still lower than expected for  $S = \frac{3}{2}$ . This deviation may again be attributed to intermolecular antiferromagnetic exchange.

During reduction of 1, the added electron is accepted in the ligand-based LUMO with contribution from Ni d orbitals, whereas the oxidation is accompanied by a structural reorganization. Figure 9 depicts the spin densities for  $1^-$ ,  $1^+$ , and  $1^{2+}$ . ADF/BP calculated spin densities on Ni are 0.216, 1.680, and 1.677 for reduced, oxidized, and doubly oxidized species, respectively, in agreement with the oxidation and spin-state combination shown in Scheme 4.



Figure 9. Spin density plots for  $1^-$ ,  $1^+$  and  $1^{2+}$  from left to right.

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Scheme 4. Conversion and spin arrangements in complexes 1<sup>n</sup>.

UV-visible-NIR spectroelectrochemistry with an optically transparent thin-layer electrolysis (OTTLE) cell and diode array detection (Figure 10) showed chemically reversible formation of  $1^+$  and then  $1^{2+}$  from 1, whereas the cathodic reduction gave only  $1^-$  as a 100% regenerable product. The reversible transition  $1/1^-$  resulted in the diminishing of the original 894 nm band and the emergence of an intense ( $\varepsilon = 10400 \text{ m}^{-1} \text{ cm}^{-1}$ ) absorption at  $\lambda_{\text{max}} = 1345 \text{ nm}$  (Figure 10, Table 5). Table 6 lists the TD-DFT-calculated singlet transitions



**Figure 10.** UV-visible-NIR spectroelectrochemistry of the steps  $1^+ \rightarrow 1^{2+}$  (top),  $1 \rightarrow 1^+$  (center), and  $1 \rightarrow 1^-$  (bottom), each in  $CH_2Cl_2/Bu_4NPF_6$  (0.1 m).

for the neutral complex **1**. The essential features in the experimental spectrum are well described by the calculations (Table 6). The assignment of individual transitions based on the frontier orbitals depicted in Figure 11 indicates that the very intense transition calculated at

Table 5. Absorption maxima. <sup>[a]</sup>			
	$\lambda_{\max}$ [nm] (10 <sup>-3</sup> × $\varepsilon$ [M <sup>-1</sup> cm <sup>-1</sup> ])		
[1] <sup>2+</sup> [1] <sup>+</sup> [1] <sup>0</sup>	891 (1.4), 525 (6.3), 431 sh (5.7), 387 (6.8), 295 sh (10.6), 227 (23.2) 893 (4.9), 721 sh (1.7), 490 (4.8), 385 (8.8), 280 sh (12.4), 227 (23.7) 894 (26.0), 715 sh (3.2), 595 sh (1.5), 446 sh (1.8), 294 (16.7), 231 (25.7)		
[1]-	1345 (10.4), 897 (3.4), 615 (1.4), 301 (14.6), 231 (25.0)		
[a] From spectroelectrochemistry in $CH_2CI_2/Bu_4NPF_6$ (0.1 M).			

914 nm has mixed intraligand/ligand-to-metal charge-transfer (IL/LMCT) character.<sup>[8,9,13,14]</sup> Calculations correctly reproduce the shift of this intense transition to longer wavelengths (1345 nm) after reduction (Figure S3 in the Supporting Information). The transition calculated for 1<sup>-</sup> at 1289 nm is formed by an excitation from the BHOMO to the BLUMO, those MOs corresponding to HOMO and LUMO of the neutral complex (Figure 11). The calculated excitation energies for the redox series of these complexes (Figures S3 and S4) qualitatively reproduce the spectral variations caused by redox changes. Based on TD-DFT calculations and on the  $[(Q_M^{-})Ni^{II}(Q_M^{-2})]^{-}$  formulation a ligandto-ligand intervalence charge-transfer (LLIVCT) transition  $\pi(Q_M^{2-}) \rightarrow \pi^*(Q_M^{\cdot-})$  is postulated. The high absorptivity reflects optimum orbital overlap in a coplanar situation. The DFT geometry optimization for  $1^-$  (Table 2) and the Nernstian behavior of the corresponding  $1/1^-$  wave support (Figure 2) the notion of maintained planarity during that redox transition with O,N-bidentate chelate ligands. Apparently, the addition of an electron does not activate the thioether S donors towards metal coordination.

In contrast, the removal of an electron in the first oxidation of 1 to  $1^+ = [(Q_M^{\bullet-})Ni^{II}(Q_M^{\bullet})]^+$  does not produce an intense low-energy-shifted absorption (Figure 8), in agreement with the non-coplanar arrangement of the redox-active  $\pi$  systems of the two now O,N,S tridentate ligands in 1<sup>+</sup>. The crystal structure (Figure 3, Table 2) shows a localized situation with one  $Q_{M}^{-}$  and one  $Q_{M}^{0}$  ligand. The second oxidation to  $\mathbf{1}^{2+}$  results in further diminished NIR absorbance (Figure 10), whereas typical<sup>[7-11]</sup> guinone transitions at about 500 nm become more intense. TD-DFT calculations qualitatively describe the diminishing intensity of the long-wavelength transition and the increasing intensity of transitions around 500-600 nm for complex ions 1<sup>+</sup> and 1<sup>2+</sup> (Figure S4 in the Supporting Information). Figure S5 and S6 in the Supporting Information, which depict MOs predominantly contributing to transitions around 550 nm indicate IL guinone character of these transitions.

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Table 6. Selected G09/PBE0/PCM calculated lowest allowed TD-DFT singlet transitions for 1 with oscillator strengths larger than 0.005.					
State	Main character [%]	Transition energies [eV] (wavelengths [nm]) calcd	Oscillator strengths calcd	$\lambda_{\max}$ [nm] (10 <sup>-3</sup> × $\varepsilon$ [M <sup>-1</sup> cm <sup>-1</sup> ]) exptl	
a¹A	99 (HOMO→LUMO)	1.36 (914)	0.519	894 (26.2)	
b <sup>1</sup> A	66 (HOMO-2→LUMO); 24 (HOMO-4→LUMO)	2.22 (557)	0.058	595 sh (1.5)	
c <sup>1</sup> A	87 (HOMO $-5 \rightarrow$ LUMO);	2.55 (485)	0.019	446 sh (1.8)	
d¹A	40 (HOMO $\rightarrow$ LUMO + 2)	3.87 (319)	0.039		
e <sup>1</sup> A	71 (HOMO-14 $\rightarrow$ LUMO); 14 (HOMO $\rightarrow$ LUMO+5)	4.21 (294)	0.048		
f <sup>1</sup> A	71 (HOMO $\rightarrow$ LUMO $+$ 5); 14 (HOMO $-$ 14 $\rightarrow$ LUMO)	4.28 (290)	0.083	294 (16.7)	
g <sup>1</sup> A	mixed	4.41 (281)	0.040		



Figure 11. The representation of FMOs of 1.

A remarkable electrolyte effect was observed for the longwavelength (NIR) band of [1](X) in  $CH_2CI_2$  or  $CH_3CN$  (Figure S7 and Table S5 in the Supporting Information). The shift from a maximum at 800 to 900 nm accompanied by significant intensity increase from  $1100 \text{ M}^{-1} \text{ cm}^{-1}$  (X = ClO<sub>4</sub> in CH<sub>2</sub>Cl<sub>2</sub>) to 8200 M<sup>-1</sup> cm<sup>-1</sup> (X = PF<sub>6</sub> in CH<sub>3</sub>CN) suggests coordinative lability in solution despite the seemingly stable configuration of [1](PF<sub>6</sub>) in the crystal (Figure 3). We assume that the oxidatively induced double S coordination in 1<sup>+</sup> is not strong enough to prevent partial dissociation; the dissociation is dependent on counterions and solvents with different coordinative and dielectric properties.

Nevertheless, the results collected in this study can be summarized in Schemes 4 and 5, showing predominantly ligandbased electron transfer, but changed coordination situations

on the metal as a consequence of the redox states of the noninnocent hemilabile ligands. The described example of reversible intramolecular double oxidative addition, based not on a metal redox process, but on ligand electron transfer, complements previous reactivity studies<sup>[5,23]</sup> where remote electron transfer at noninnocent ligands has activated addition reactions at the metal or at the ancillary ligand. This present example of nickel complexes thus complements previous related studies of copper,<sup>[3]</sup> iridium,<sup>[6, 24]</sup> ruthenium, and rhodium compounds<sup>[24]</sup> and may be extended to complexes of



Scheme 5. Assignment of oxidation states in the redox series of 1<sup>n</sup>.

other metals. Dinickel complexes of redox-active quinonoid bischelate ligands, which have been well investigated by Braunstein et al.,<sup>[25]</sup> might thus be modified accordingly in order to add another dimension to the systems described here.

# **Experimental Section**

# General

Commercially available compounds were purchased from Aldrich and used as received. Solvents for the complexes were dried with standard Schlenk techniques. 2-(Methylthiomethyl)aniline was prepared according to a reported procedure.<sup>[26]</sup> Purification was car-



ried out by column chromatography (silica gel,  $CH_2Cl_2$ /pentane, 1:1).

#### Instrumentation

<sup>1</sup>H NMR spectra were obtained with a AV250 spectrometer from Bruker. UV-visible-NIR spectra were recorded on a Shimadzu UV 160 spectrometer. UV-visible-NIR spectroelectrochemical studies were performed in CH<sub>2</sub>Cl<sub>2</sub>/Bu<sub>4</sub>NPF<sub>6</sub> (0.1 M) at 298 K by using an optically transparent thin layer electrochemical (OTTLE) cell<sup>[27a]</sup> in connection with a J&M TIDAS spectrophotometer. The EPR measurements were made with a Bruker EMX spectrometer (9.5 GHz), with a two-electrode cell.<sup>[27b]</sup> Magnetic susceptibility measurements were carried out with a Quantum Design MPMS SQUID magnetometer. Temperature-dependent magnetization between 1.8-350 K was measured in 500 Oe external field. Experimental magnetic susceptibilities were corrected with the help of Pascal's tables. Cyclic voltammetric measurements were carried out with a M273A potentiostat and a function generator M175 from EG&G. Platinum working and auxiliary electrodes and silver wire as pseudoreference electrode were used in a three-electrode configuration. The supporting electrolyte was Bu<sub>4</sub>NPF<sub>6</sub> (0.1 M) and the solute concentration was about  $10^{-3}$  M. The ferrocenium/ferrocene couple Fc<sup>+/0</sup> was used as internal reference.<sup>[28]</sup> Elemental analysis was carried out with a Perkin-Elmer Analyzer 240. Electrospray mass spectra were recorded on a Bruker Daltronics Microtof Q spectrometer. Xray diffraction was performed with a Bruker Kappa Apex II Duo system. The structures were solved and refined by full-matrix leastsquares techniques on F<sup>2</sup> by using the SHELX-97 program.<sup>[29]</sup> The absorption corrections were done numerically or by the multiscan technique. All data were corrected for Lorentz and polarization effects, and the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the refinement process as per the riding model.

### Synthesis of 4,6-di-*tert*-butyl-2-(2-methylthiomethylphenyl)aminophenol

2-(Methylthiomethyl)aniline (3.06 g, 20.0 mmol) and 3,5-di-*tert*-butylcatechol (4.45 g, 20.0 mmol) were refluxed for eight hours in dry *n*-hexane (60 mL) with NEt<sub>3</sub> (0.8 mL) under an argon atmosphere. The solvent was removed at 70 °C and the oily residue was dissolved in *n*-hexane (2 mL). After seven days at -4 °C the solvent was removed and the brown oil was subjected to chromatography on a silica gel column with diethylether/*n*-pentane (5:95) as eluent. The desired product was found in the second fraction. Yield: 3.4 g (10 mmol, 50%). <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>, 303 K):  $\delta$  (ppm) = 1.28 (s, 9 H, *CH*<sub>3</sub>), 1.44 (s, 9 H, *CH*<sub>3</sub>), 2.06 (s, 3 H, SCH<sub>3</sub>), 3.83 (s, 2 H, SCH<sub>2</sub>), 5.93 (brs, 1 H, OH), 6.25 (brs, 1 H, NH), 6.46–6.50 (m, 1 H, Ar-H), 6.76 -6.82 (m, 1 H, Ar-H), 7.01 (d, <sup>4</sup>J<sub>H-H</sub>=2.3 Hz, 1 H, Cat-H); TMRS (ESI): *m/z*: 380.2011 [*M*+Na]<sup>+</sup> (calcd *m/z*: 380.2019).

# Synthesis of bis(4,6-di-*tert*-butyl-*N*-(2-methylthiomethylphenyl)iminosemiquinonato)-nickel(II) (1)

#### 4,6-Di-tert-butyl-2-((2-methylthiomethylphenyl)amino)-phenol

(358 mg, 1.00 mmol) and NiCl<sub>2</sub>×6 H<sub>2</sub>O (119 mg, 0.50 mmol) were refluxed with NEt<sub>3</sub> (0.28 mL) in dry acetonitrile (10 mL) for two hours under an atmosphere of argon. The light green solid was filtered and suspended in CHCl<sub>3</sub>. After 10 min, the dark-green solution was filtered and the solvent was removed under reduced pressure. The residue was dissolved in *n*-pentane and filtered to remove HNEt<sub>3</sub>Cl. After removal of the solvent, the dark-green solid

was recrystallized from hot acetonitrile. Yield: 122 mg (0.16 mmol, 32%). <sup>1</sup>H NMR (250 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 303 K):  $\delta$  (ppm)=1.03 (s, 18 H, CH<sub>3</sub>), 1.08 (s, 18H, CH<sub>3</sub>), 1.98 (s, 6H, SCH<sub>3</sub>), 3.70-4.38 (brm, 4H, SCH<sub>2</sub>), 6.17–7.62 (brm, 12H, Ar-H and SQ-H); <sup>1</sup>H NMR (400 MHz,  $[D_8]$ toluene, 223 K):  $\delta$  (ppm) = 1.08 (s, 10.8 H, CH<sub>3</sub>), 1.11 (s, 7.2 H, CH<sub>3</sub>), 1.27 (s, 7.2H, CH<sub>3</sub>), 1.31 (s, 10.8H, CH<sub>3</sub>), 1.64 (s, 2.4H, SCH<sub>3</sub>), 1.74 (s, 3.6 H, SCH<sub>3</sub>), 3.87 (d,  ${}^{1}J_{H-H} = 14.0$  Hz, 0.8 H, SCH<sub>2</sub>), 3.93 (d,  $^{1}J_{H-H} = 14.0 \text{ Hz}, 1.2 \text{ H}, \text{ SCH}_{2}$ ), 4.46 (d,  $^{1}J_{H-H} = 14.0 \text{ Hz}, 1.2 \text{ H}, \text{ SCH}_{2}$ ), 4.54 (d,  ${}^{1}J_{H-H} = 14.0$  Hz, 0.8 H, SCH<sub>2</sub>), 6.64 (s, 1.2 H, SQ-H), 6.67 (s, 0.8 H, SQ-H), 7.07 (d,  $J_{H-H} = 7.74$  Hz, 0.8 H, Ar-H), 7.15 (d,  $J_{H-H} =$ 7.74 Hz, 1.2 H, Ar-H), 7.20-7.26 (m, 4H, Ar-H and SQ-H), 7.35 (d,  $J_{\rm H-H}$  = 7.74 Hz, 1.2 H, Ar-H), 7.42 (d,  $J_{\rm H-H}$  = 7.74 Hz, 0.8 H, Ar-H), 7.47 (d, J<sub>H-H</sub>=7.74 Hz, 1.2 H, Ar-H), 7.60 (d, J<sub>H-H</sub>=7.74 Hz, 0.8 H, Ar-H); elemental analysis calcd (%) for  $C_{44}H_{58}N_2NiO_2S_2$ : C 68.65, H 7.59, N 3.64; found: C 68.66, H 7.65, N 3.67; HRMS (ESI): m/z: 768.3262  $[M]^+$  (calcd m/z: 768.3288). Two different kinds of single crystals for X ray diffraction were grown either out of a dichloromethane/ methanol mixture at room temperature or from acetonitrile at 0°C.

#### Synthesis of $[1]X (X^-: PF_6^-, CIO_4^-)$

**CAUTION:** PERCHLORATE SALTS CAN DECOMPOSE EXPLOSIVELY AND SHOULD BE HANDLED WITH CARE. Compound 1 (38 mg, 0.05 mmol) and AgX (0.05 mmol) were dissolved in dry  $CH_2CI_2$ (5 mL) and stirred for one hour. The solution was filtered, concentrated and layered with dry *n*-hexane (10 mL). After filtration, the solid was dried in vacuo. Elemental analysis calcd (%) for [1] $CIO_4^-$ ( $C_{44}H_{58}CIN_2NiO_6S_2 \times 0.6 CH_2CI_2$ ): C 58.01, H 6.47, N 3.03; found: C 58.04, H 6.40, N 3.04. Single crystals could be obtained through slow diffusion of hexane into a dichloromethane solution of the hexafluorophosphate complex in the presence of a silver wire.

### Synthesis of [1](ClO<sub>4</sub>)<sub>2</sub>

Compound 1 (77 mg, 0.1 mmol) and AgClO<sub>4</sub> (45 mg, 0.2 mmol) were dissolved in dry  $CH_2Cl_2$  (8 mL) and stirred for five hours. The solution was filtered, concentrated, and layered with dry *n*-hexane (10 mL). After filtration, the solid was dried in vacuo. Elemental analysis calcd (%) for  $C_{44}H_{58}Cl_2N_2NiO_{10}S_2$ : C 54.56, H 6.04, N 2.89; found: C 54.42, H 6.10, N 2.95. Cyclic voltammetry showed essentially the same response as that of [1](ClO<sub>4</sub>), the UV-visible-NIR spectrum represents that observed by spectroelectrochemistry of 1 (see Figure 8). Susceptibility measurements up to 300 K revealed values < 2.3  $\mu_{8}$ . Single crystals were obtained from [1](ClO<sub>4</sub>) through disproportionation, which takes place during the slow diffusion of hexane into a dichloromethane solution of the monocation in the absence of a silver wire.

### Quantum chemical calculations

The electronic structures of  $1^n = [Ni(Q_M)_2]^n$  (n = -1, 0, 1, 2) were calculated by DFT methods by using the Gaussian  $09^{[30]}$  and Amsterdam Density Functional (ADF2013.01)<sup>[31,32]</sup> program packages. G09 calculations employed the Perdew, Burke, Ernzerhof<sup>[33,34]</sup> PBE0 hybrid functional (G09/PBE0). The geometry of the open-shell systems was calculated by the UKS approach. Geometry optimization was followed by vibrational analysis in order to characterize stationary states and enumerate free energies  $\Delta G$ . For H and C atoms polarized triple- $\zeta$  basis sets 6–311G(d), together with polarized triple- $\zeta$  basis sets 6–311G(d), together with polarized triple- $\zeta$  basis sets 6–311G(d) for N, O, S, and Ni were used.<sup>[35]</sup> Electronic excitations were calculated by TD-DFT with polarizable continuum model (PCM)<sup>[36]</sup> solvent correction.

Within the ADF program, Slater type orbital (STO) basis sets of triple- $\zeta$  quality with two polarization functions for Ni, C, N, O, and

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S atoms and double- $\zeta$  with one polarization function for H atom were employed. Inner shells were represented by the frozen core approximation (1s for C, N, and O; 2p for S and Ni were kept frozen). Within ADF the functional including Becke's gradient correction to the local exchange expression in conjunction with Perdew's gradient correction to local density approximation (LDA) with VWN parameterization of electron gas data was used (ADF/ BP86).<sup>[37,38]</sup>

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