Cobalt(II)/(III) Complexes Containing *o*-Iminothiobenzosemiquinonato(1−) and *o*-Iminobenzosemiquinonato(1−) π-Radical Ligands

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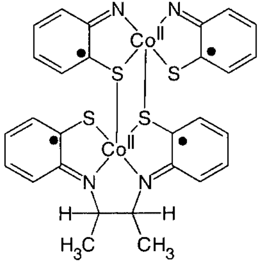
The coordination chemistry of 6-amino-2,4-di-*tert*-butylthiophenol (H[L_S^{AP}]) and of 2-anilino-4,6-di-*tert*-butylphenol (H[L_O^{AP}]) with cobalt(II) ions was investigated in the presence and absence of dioxygen. It was shown that both compounds were redox-non-innocent ligands, existing in different protonation and oxidation levels as: (i) *o*-aminophenolates(1–) [$(L_X^{AP})^{1-}$], (ii) *o*-imidophenolates(2–) [$(L_X^{IP})^{2-}$], and (iii) one-electron oxidized forms *o*-iminobenzosemiquinonates(1–) [$(L_X^{ISQ})^{1-}$], which are π-radicals (X = S, O for the sulfur or oxygen derivative). The following complexes were synthesized: [$Co^{II}(L_S^{AP})_2]_2$ (**1**), [$Co^{II}(L_S^{ISQ})_2]_2 \cdot 0.5n$-hexane (**2**·0.5*n*-hexane), [$Co^{III}I(L_S^{ISQ})_2$] (**3**), [$Co^{III}I(L_O^{ISQ})_2$] (**4**), and [$Co^{III}Cl(L_O^{ISQ})_2$] (**5**). The compounds **2**·0.5*n*-hexane, **4**, and **5** were structurally characterized by X-ray crystallography. It was shown that the different protonation and oxidation levels of the ligands could readily be identified by X-ray crystallography. Complex **2** could be reversibly oxidized and reduced electrochemically, yielding a monocation and a monoanion, respectively. It was shown that these processes were metal-centered ([$Co^{III}(L_S^{ISQ})_2]^+$, [$Co^{II}(L_S^{ISQ})_2$], and [$Co^{I}(L_S^{ISQ})_2]^-$). The electronic structures were elucidated by UV/Vis and EPR spectroscopy and magnetochemistry. Complexes **3**, **4**, and **5** were shown to be singlet diradicals.

1. Introduction

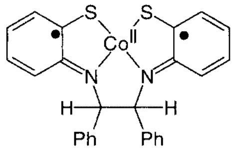
Despite a recent assertion to the contrary,[1] *N*,*S*-coordinated *o*-aminothiophenolate ligands are redox-non-innocent in the sense that they can exist at four distinctly different protonation and oxidation levels (Scheme 1).[2] We have recently shown that the monomeric diamagnetic, square-planar complexes [$M^{II}(L_S^{ISQ})_2$] (M = Ni, Pd, Pt) contain two *N*,*S*-coordinated *o*-iminothiobenzosemiquinonato(1−) π-radical ligands [$(L_S^{ISQ})^{1-}$], which are strongly antiferromagnetically coupled intramolecularly.[2] The species are thus considered to be diradicals with singlet ground states.

As shown in Scheme 2, the geometrical differences between *N*,*S*-coordinated *o*-aminothiophenolato(1−) [$(L_S^{AP})^{1-}$], *o*-imidothiophenolato(2−) [$(L_S^{IP})^{2-}$], and their monoanionic radical form $(L_S^{ISQ})^{1-}$ can readily be identified by X-ray crystallography. The same has been shown to hold for *O*,*N*-coordinated *o*-aminophenolates [$(L_O^{AP})^{1-}$], *o*-imidophenolate(2−) [$(L_O^{IP})^{2-}$], and *o*-iminobenzosemiquinonate(1−) radicals [$(L_O^{ISQ})^{1-}$].[3−7] In these and in the current study, the ligands used were Sellmann's 6-amino-2,4-di-*tert*-butylthiophenol[8] (H[L_S^{AP}]) and 2-anilino-4,6-di-*tert*-butylphenol[4] (H[L_O^{AP}]). Here we report the coordination chemistry of cobalt(II) and -(III) with these ligands (Scheme 3).

Coordination of the unsubstituted *o*-aminothiophenol with cobalt(II) in the absence of air yielded orange-brown, paramagnetic [$Co^{II}(SC_6H_4NH_2)_2]_2$. Its dimeric nature was inferred from the temperature dependence of its magnetic moment, yielding an $S_t = 0$ ground state from two antiferromagnetically coupled high-spin Co^{II} ions ($S_{Co} = {}^3/_2$). In the presence of oxygen a deep blue material was obtained [$Co^{II}(SC_6H_4NH)_2$], but its exact nature was not established. Finally, a diamagnetic green [$Co^{III}(SC_6H_4NH_2)_3$] species was reported. None of these species was structurally characterized, and the problems of differing oxidation and protonation levels were not considered.[9,10] Recently, Artaud et al.[11] reported a structurally characterized dinuclear



S = 0, ref. [11]



S = 1/2, ref. [12]

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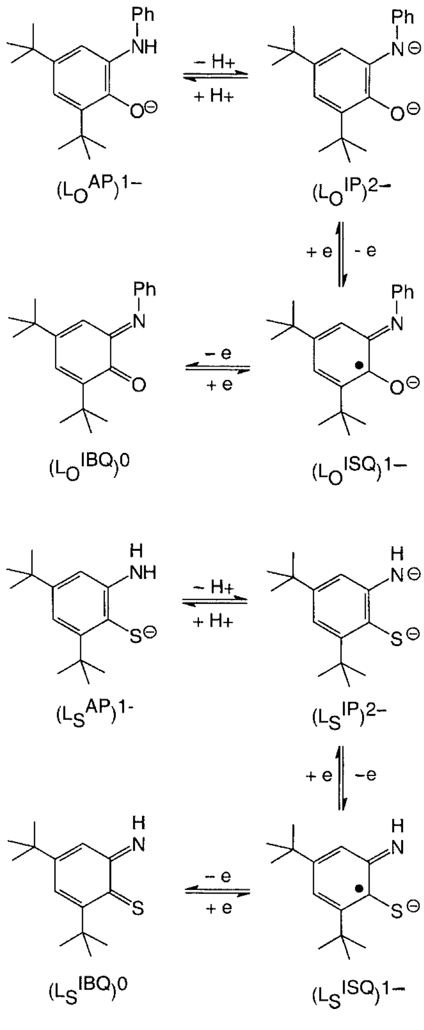
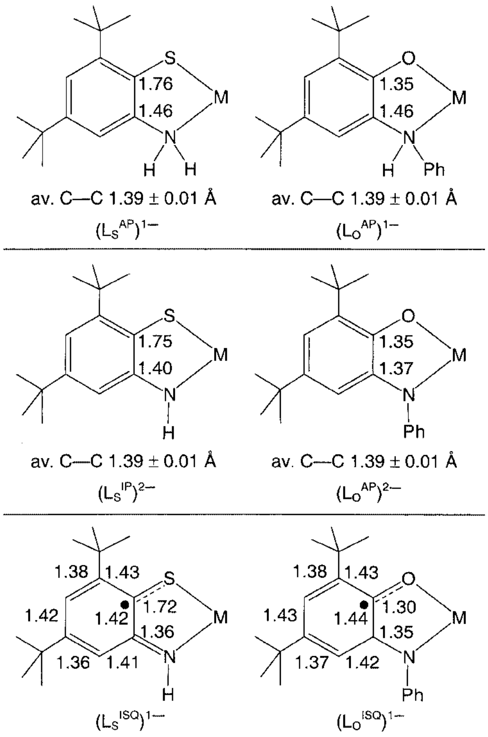


Scheme 1



Scheme 2

Complexes:

$[Co^{II}(L_S^{AP})_2]_2$ (**1**)
$[Co^{II}(L_S^{ISQ})_2]_2$ (**2**)
$[Co^{III}I(L_S^{ISQ})_2]$ (**3**)
$[Co^{III}I(L_O^{ISQ})_2]$ (**4**)
$[Co^{III}Cl(L_O^{ISQ})_2]$ (**5**)

Scheme 3

complex of cobalt(II) with the ligand 2,3-bis(2-mercaptoanilino)butane, which is very similar to the bis(phenyl) analogue reported by Kawamoto, Kuma, and Kushi.[12] We show here for the first time that both compounds contain *N,S*-coordinated *o*-iminothiobenzosemiquinonate(1−) π-radicals.

2. Results and Discussion

2.1. Synthesis and Characterization of Complexes

2.1.1. Complex 1

Treatment of the ligand 6-amino-2,4-di-*tert*-butylthiophenol[8] ($H[L_S^{AP}]$) with $CoCl_2$ (2:1) in dry acetonitrile under strictly anaerobic conditions produced, upon addition of 2 equiv. of the base triethylamine, an orange precipitate of $[Co^{II}(L_S^{AP})_2]_2 \cdot 2CH_3CN$ (**1**·$2CH_3CN$) in good yields. This material was extremely air-sensitive even in the solid state and had to be stored under argon.

In the infrared spectrum of **1**, an antisymmetric and two symmetric ν(N−H) stretching frequencies were observed: at 3322 and at 3268 and 3246 cm^{-1}, respectively. This clearly indicated the presence of two *N*-coordinated amino groups ($R-NH_2$) in **1**. The electronic spectrum of **1** measured in CH_2Cl_2 solution displayed no intense absorption maxima > 450 nm ($\varepsilon > 10^3$ M^{-1} cm^{-1}), indicating that the ligand was aromatic and that it was *N,S*-coordinated as the monoanion $(L_S^{AP})^{1-}$.

Complex **1** was paramagnetic. Figure 1 displays the temperature dependence of the magnetic moment of **1**. It was possible to fit the data to a dimer model with $S_{Co} = {}^3/_2$ by use of the spin Hamiltonian $H = -2J\, S_1 \cdot S_2$ ($S_1 = S_2 = {}^3/_2$). The following parameters yielded a satisfactory fit: $g_{Co} = 2.2$, $J = -144$ cm^{-1}, $\chi_{TIP} = 0.95 \times 10^{-3}$ e.m.u., and 1% of a paramagnetic impurity ($S = {}^3/_2$). Thus, a strong intramolecular antiferromagnetic coupling between two mononuclear units $Co^{II}(L_S^{AP})_2$ prevailed, yielding an $S = 0$ ground state. In agreement with this, the X-band EPR spectrum of a toluene solution of **1** at 10 K displayed a signal ($g = 4.3$) typical for an $S = {}^3/_2$ ground state of the mononuclear unit. Thus, in solution, dimeric **1** was in equilibrium with its monomer. For the dimer in the solid state we propose one of the two following structures, depending on the relative configuration of the two $(L_S^{AP})^{1-}$ ligands to each other in a monomer that can be *trans* or *cis*. The spectroscopic and magnetic properties of **1** were quite similar to those reported for $[Co^{II}(abt)_2]$,[9] "abt^{1-}" representing the unsubstituted *o*-aminothiophenolate(1−) anion.

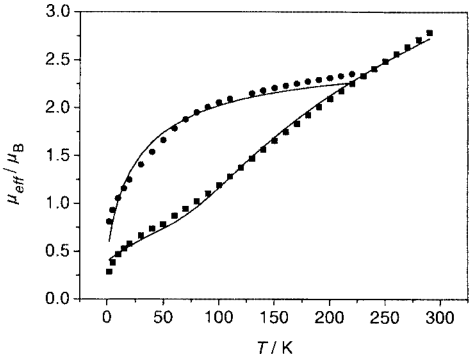
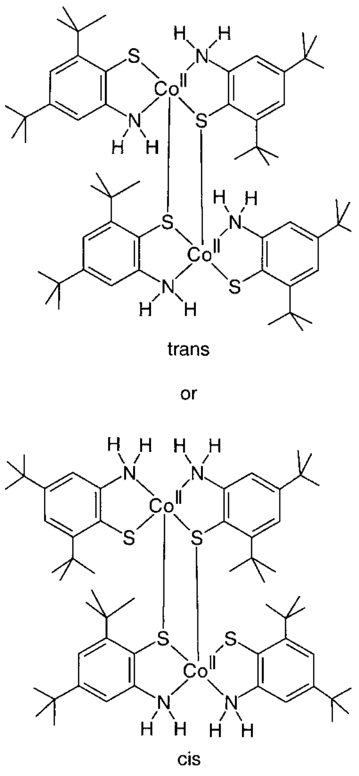


Figure 1. Temperature dependence of the magnetic moment of dinuclear **1** (■) and **2** (●); the solid lines represent best fits by use of the parameters given in the text

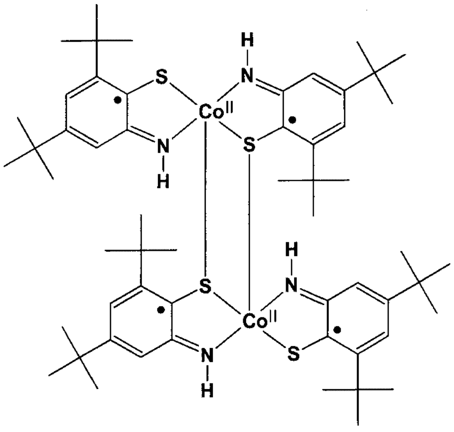


1

2.1.2. Complex 2

When orange-red crystals of **1** were exposed to air at 20 °C, a rapid color change to black was observed. Dissolution of this material in CH_2Cl_2 under argon produced a deep blue solution, from which black crystals of $[Co^{II}(L_S^{ISQ})_2]_2$·0.5*n*-hexane (**2**·0.5*n*-hexane) were obtained upon addition of *n*-hexane.

In the infrared spectrum of **2**, only a single N−H stretching frequency (at 3296 cm^{-1}) was observed, as to be expected for an imino group. The temperature dependence of the magnetic susceptibility of a solid sample of the dimeric species **2** was recorded in the range 4−240 K. The effective magnetic moment varied between 0.65 μ_B at 10 K and 1.6 μ_B at 240 K (per Co). This behavior was consistent with the presence of two Co^{II} ions with $S = {}^1/_2$, weakly antiferromagnetically coupled to yield an $S_t = 0$ ground state. From a fit of the data shown in Figure 1, $J = -7$ cm^{-1} was calculated. The X-band EPR spectrum of a frozen toluene solution of **2** at 10 K displayed an $S = {}^1/_2$ signal at $g \approx 2$, indicating that dimeric **2** existed in solution in equilibrium with its monomer. In agreement with the results of an X-ray structure determination (see below), we assigned the following structure to **2**.

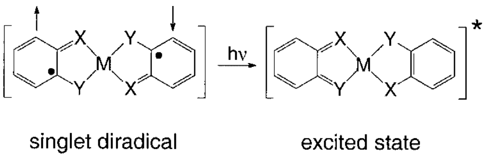


2

It thus appeared that **2** was the four-electron oxidation product of **1**, as in Equation (1).

$$[Co^{II}(L_S^{AP})_2]_2 + O_2 \rightarrow [Co^{II}(L_S^{ISQ})_2]_2 + 2\,H_2 \qquad (1)$$

The electronic spectrum of **2** in CH_2Cl_2 solution at 25 °C, shown in Figure 2, displayed a very intense ($\varepsilon > 10^4$ M^{-1} cm^{-1}) absorption at 673 nm, responsible for the deep blue color of **2**, which was absent in the spectrum of **1**. This band corresponded to a spin- and dipole-allowed transition observed for all square-planar complexes containing two *cis* or *trans X,Y*-coordinated radicals.[2,4,13]



All the spectroscopic data of **2** thus pointed to the presence of two *N,S*-coordinated *o*-iminothiobenzosemiquinonato(1−) π-radicals in a monomeric subunit with an $S = {}^1/_2$ ground state.

Interestingly, we discovered that the electronic spectrum of **2** in CH_2Cl_2 (or in methylcyclohexane) was temperature-dependent. Upon cooling from +25 to −70 °C, the intense band at 673 nm disappeared, but was regenerated upon

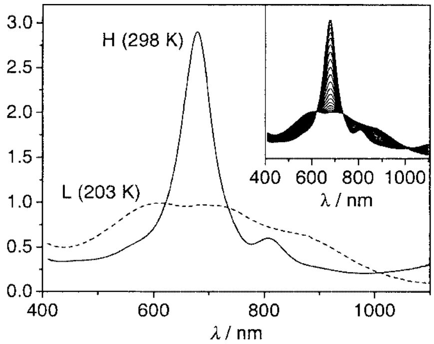


Figure 2. Electronic spectra of the high-temperature form (H) of **2** (at 25 °C) and of its low-temperature form (L) at −70 °C (absorption coefficients are calculated per cobalt ion); the inset shows the temperature dependence of the spectra between 25 and −70 °C (in 5 °C steps)

warming. Figure 2 shows the spectra of the high- and low-temperature forms. We analyzed these spectral changes on the assumption of the equilibrium shown in Equation (2) and calculated the following thermodynamic data: $\Delta G^{300} = -4.3$ kJ mol^{-1}, $\Delta H = 35 \pm 2$ kJ mol^{-1}, $\Delta S = 131 \pm 7$ J mol^{-1} K^{-1} (in methylcyclohexane) and $\Delta G^{300} = -3.6$ kJ mol^{-1}, $\Delta H = 33 \pm 2$ kJ mol^{-1}, $\Delta S = 122 \pm 9$ J mol^{-1} K^{-1} (in dichloromethane).

$$[\mathrm{Co^{III}(L_S{}^{IP})(L_S{}^{ISQ})}]_2 \overset{K}{\rightleftarrows} [\mathrm{Co^{II}(L_S{}^{ISQ})_2}]_2 \qquad (2)$$

Similar valence tautomeric equilibria have been reported by Pierpont et al.[14−16] for (catecholato)cobalt(III) and (semiquinonato)cobalt(II) complexes, as shown in Equation (3). For this equilibrium, $\Delta G^{300} = -3.3$ kJ mol^{-1}, $\Delta H = 33.9(1)$ kJ mol^{-1}, and $\Delta S = 124(1)$ J mol^{-1} K^{-1} were reported [bpy represents the ligand 2,2′-bipyridine, (DBSQ)$^{1-}$ is either 3,5- or 3,6-di-*tert*-butyl-1,2-benzosemiquinonate(1−), and (DBCat)$^{2-}$ is the corresponding one-electron reduced catecholate(2−)].

$$[\mathrm{Co^{III}(bpy)(DBSQ)(DBCat)}] \rightleftarrows [\mathrm{Co^{II}(bpy)(DBSQ)_2}] \qquad (3)$$

It should be noted that the valence tautomeric equilibrium (2) was only observed in solution. In the solid state, the electronic spectrum of **2** did not change over the temperature range 10−300 K. This was also in qualitative agreement with the observations of Pierpont et al. on the [Co$^{\mathrm{II}}$(bpy)(DBSQ)$_2$] system. They reported that the transition temperature was about 50 °C higher in the solid state than in solution. They also concluded that "changes in bond energy and vibrational frequency associated with the electron transfer step are the primary contributors to the thermodynamic changes of the equilibrium". The above results for **2** represent the first example of valence tautomers of an *N*,*S*-coordinated *o*-aminothiophenolate complex.

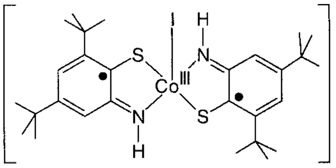
Interestingly, Pierpont's tautomers involved octahedral cobalt(II)/(III) complexes in which the transition from a low-spin cobalt(III) (d^6, $S = 0$) to a high-spin cobalt(II) (d^7, $S = {}^3/_2$) configuration was accompanied with increasing temperature by a net change of the effective magnetic moment from 1.7 μ_B for the cobalt(III) form ($S_t = {}^1/_2$) to ca. 5.5 μ_B for the cobalt(II) form. In contrast, equilibrium (2) was not associated with a similar net change of the effective magnetic moment with increasing temperature. Both monomeric subunits [Co$^{\mathrm{III}}$(L$_{\mathrm{S}}^{\mathrm{IP}}$)(L$_{\mathrm{S}}^{\mathrm{ISQ}}$)] and [Co$^{\mathrm{II}}$(L$_{\mathrm{S}}^{\mathrm{ISQ}}$)$_2$] possessed an $S = {}^1/_2$ ground state, which may antiferromagnetically couple to an overall diamagnetic ground state in the dimers.

2.1.3. Complex 3

Treatment of **2**, in CH_2Cl_2 under Ar, with I_2 (1:1) dissolved in *n*-hexane changed the blue color to dark green. From this solution a dark green microcrystalline residue of [Co$^{\mathrm{III}}$I(L$_{\mathrm{S}}^{\mathrm{ISQ}}$)$_2$] (**3**) was obtained in good yields [Equation (4)].

$$[\mathrm{Co^{II}(L_S^{ISQ})_2}]_2 + \mathrm{I_2} \rightarrow 2[\mathrm{Co^{III}I(L_S^{ISQ})_2}] \qquad (4)$$

Complex **3** is diamagnetic ($S = 0$), as judged from its "normal" ^{1}H NMR spectrum. In the infrared spectrum, a single N−H stretching frequency was observed at 3231 cm^{-1}, indicating the presence of two equivalent imino groups. Figure 3 shows the electronic spectrum of **3** in CH_2Cl_2 solution. The very intense absorption at 641 nm ($\varepsilon = 1.7 \times 10^4$ M^{-1} cm^{-1}) was again indicative of the presence of two (L$_{\mathrm{S}}^{\mathrm{ISQ}}$)$^{1-}$ π-radical ligands. We therefore propose the following structure for **3**.



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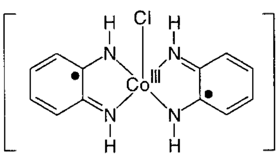


[Co$^{\mathrm{III}}$Cl(s-bqdi)$_2$] ref. [17]

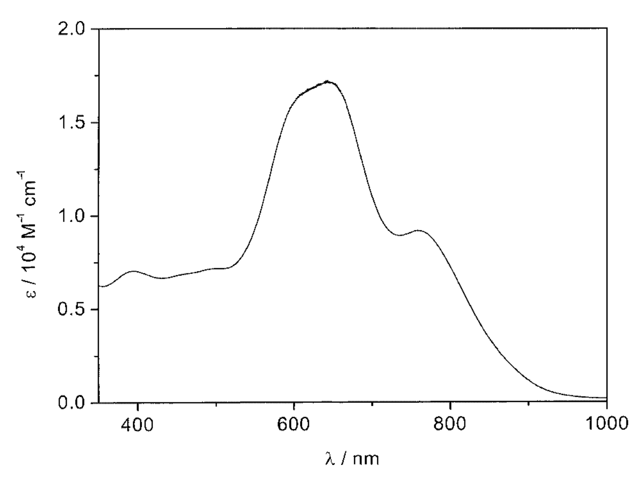


Figure 3. Electronic spectrum of **3** in CH_2Cl_2 solution at 20 °C

This complex is analogous to diamagnetic [$Co^{III}Cl(s\text{-}bqdi)_2$], which has been structurally characterized.[17] The ligand $(s\text{-}bqdi)^{1-}$ is the *N,N*-coordinated *o*-diiminobenzosemiquinonate(1−) π-radical.

2.1.4. Complexes 4 and 5

Treatment of 2-anilino-4,6-di-*tert*-butylphenol ($H[L_O^{AP}]$) in acetonitrile with CoI_2 (ca. 2:1) in the presence of air and triethylamine as base resulted in the precipitation of dark microcrystalline [$Co^{III}I(L_O^{ISQ})_2$] (**4**). This compound is the exact sulfur-free analogue of **3**. Note that, in contrast to **3**, compound **4** was formed with oxygen as the sole oxidant.

Complex **4** is also diamagnetic ($S = 0$). Figure 4 shows the electronic spectrum of **4** dissolved in CH_2Cl_2. The intense absorption maxima at 695 nm ($\varepsilon = 1.87 \times 10^4$ M^{-1} cm^{-1}) and 884 nm (1.03×10^4 M^{-1} cm^{-1}) were again indicative of the presence of two *O,N*-coordinated $(L_O^{ISQ})^{1-}$ π-radical ligands.

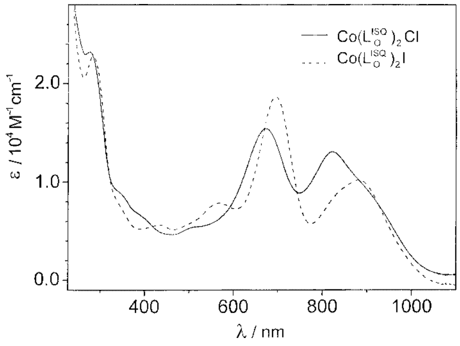
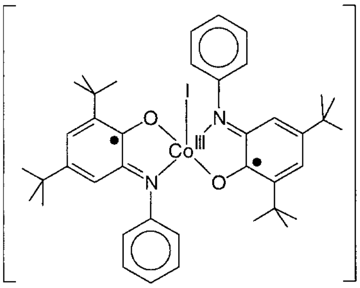


Figure 4. Electronic spectra of **4** and **5** in CH_2Cl_2 solution at 20 °C



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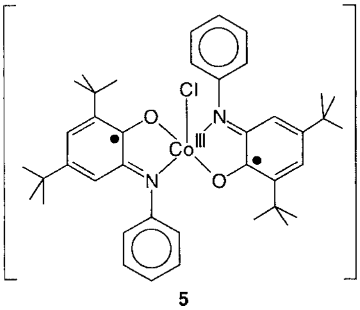


5

In an attempt to generate the exact analogue of **2**, the reaction between [$Co(H_2O)_6$]$(BF_4)_2$ and $H[L_O^{AP}]$ (1:1) and NEt_3 in CH_3CN in the presence of air was studied. A dark solid obtained from this reaction mixture was recrystallized from a $CH_3CN/CHCl_3$ (1:1) mixture, yielding single crystals of [$Co^{III}Cl(L_O^{ISQ})_2$] (**5**). Note that the coordinated chloride ion in **5** had to have been abstracted from chloroform. Complex **5** is also diamagnetic, and isostructural with **4**. Complex **5** could also be synthesized more straightforwardly by employment of the method used to prepare **4** by use of $CoCl_2$ as starting material. The corresponding cobalt halide for the preparation of **4** and **5** was employed only in slight excess over the amount of ligand (ca. 1:1 and not 1:2 as required stoichiometrically) in order to avoid the formation of the known octahedral complex [$Co^{III}(L_O^{ISQ})_3$].[3]

2.2. Crystal Structures

The crystal structures of complexes **2**·0.5*n*-hexane, **4**, and **5** were determined by single-crystal X-ray crystallography at 100 K, and for **2** also at 295 K. Figure 5 shows the structure of the neutral dimer in crystals of **2**, whereas the structures of the mononuclear, neutral molecules in crystals of **4** and **5** are both displayed in Figure 6. Selected bond lengths are summarized in Table 1.

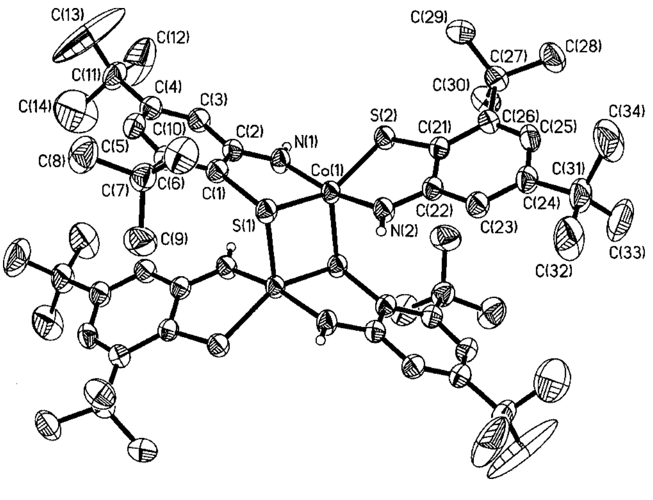


Figure 5. Structure of the neutral dimer in crystals of **2**·0.5*n*-hexane at 293 K; thermal ellipsoids are drawn at the 40% probability level; small open circles are observed hydrogen atoms of the imine groups; all other H atoms are omitted

We describe the structures of **4** and **5** first, because previous structural work on *O,N*-coordinated *o*-iminobenzosemiquinonato π-radical complexes such as the octahedral [$M(L_O^{ISQ})_3$] (M = Co^{III},[3] Cr^{III},[5] Fe^{III} [5]), the square-planar [$M(L_O^{ISQ})_2$] (M = Cu^{II}, Ni^{II}, Pd^{II}, Pt^{II}),[4] or the square-planar [$M(L_O^{ISQ})(bpy)$]PF_6 (M = Pd^{II}, Pt^{II})[7] has allowed the unequivocal structural characterization of the $(L_O^{ISQ})^{1-}$ radical anion. In all these structures the geometrical features of the ligand are identical within the small experimental error of ±0.01 Å (3σ): (i) the C−O and C−N distances are short at 1.30 Å and 1.35 Å, respectively, and (ii) the C−C distances in the six-membered ring invariably show a quinoid-type distortion, with two short C−C distances at 1.37 Å and four longer ones at ca. 1.42 Å. Furthermore, for the neutral species [$M(L_O^{IP})(bpy)$] (M = Pd^{II},

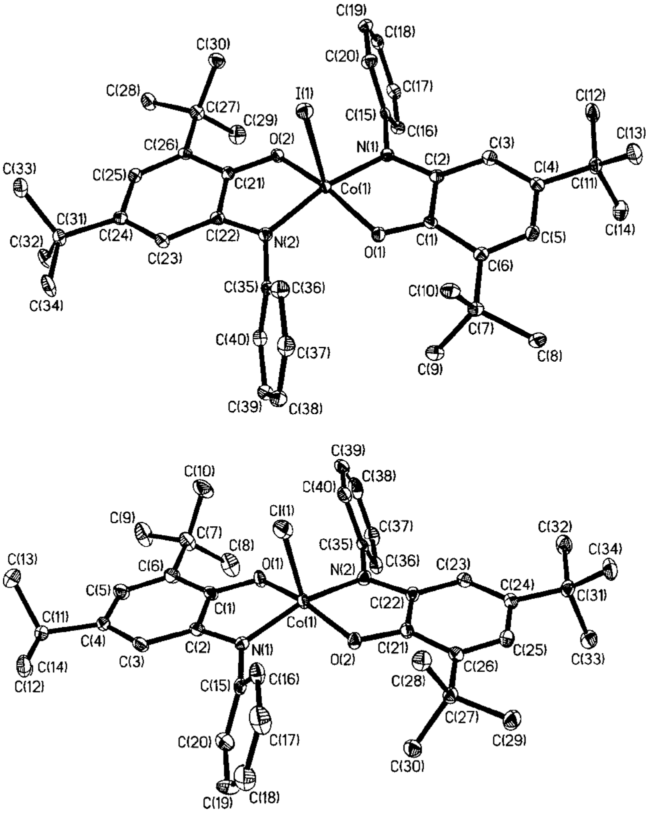
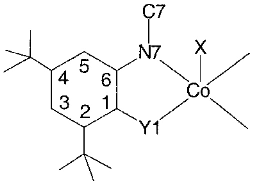


Figure 6. Structures of the neutral molecules in crystals of **4** (top) and **5** (bottom)

Table 1. Selected bond lengths [Å]

	2	**4**		**5**	
M−X	2.3506(9)	2.5784(4)		2.265(1)	
M−N1	1.866(2)	1.864(2)		1.870(3)	
M−N2	1.843(2)	1.857(2)		1.862(3)	
M−Y1	2.2015(9)	1.862(2)		1.856(2)	
M−Y2	2.1525(9)	1.873(2)		1.869(3)	
Terminal ligand(s)					
N1−C6	1.338(4)	1.355(3)	1.349(3)	1.346(5)	1.344(5)
N1−C7	−	1.433(3)	1.435(3)	1.426(5)	1.439(4)
Y1−C1	1.720(3)	1.294(3)	1.300(3)	1.301(5)	1.304(4)
C1−C6	1.419(4)	1.432(3)	1.436(3)	1.429(5)	1.429(6)
C1−C2	1.428(4)	1.444(3)	1.437(3)	1.435(5)	1.430(5)
C2−C3	1.366(4)	1.370(3)	1.372(3)	1.368(6)	1.374(6)
C3−C4	1.420(5)	1.442(3)	1.439(3)	1.422(6)	1.442(5)
C4−C5	1.363(4)	1.374(3)	1.370(3)	1.363(5)	1.366(6)
C5−C6	1.422(4)	1.418(3)	1.424(3)	1.438(5)	1.424(5)
Bridging ligand					
N1−C6	1.348(4)				
S1−C1	1.751(3)				
C1−C6	1.426(4)				
C1−C2	1.404(4)				
C2−C3	1.363(5)				
C3−C4	1.414(5)				
C4−C5	1.384(4)				
C5−C6	1.422(4)				



	X	Y
2	S	S
4	I	O
5	Cl	O

$\mathrm{Pt^{II}}$),[7] we have clearly established by X-ray crystallography that the *O*,*N*-coordinated dianion $(\mathrm{L_O^{IP}})^{2-}$ has distinctly different geometrical features. The C−O and C−N distances are significantly longer, at 1.35 and 1.39 Å, respectively, and the C−C distances of the now aromatic ring are equal, at 1.39 Å. These parameters are given in Scheme 2.

It is now immediately evident from the data in Table 1 and Scheme 2 that both organic ligands in **4** and **5** are *O*,*N*-coordinated, monoanionic π-radicals $(\mathrm{L_O^{ISQ}})^{1-}$. The electronic structures of **4** and **5** may therefore correctly be described as singlet diradical, each containing a low-spin, diamagnetic, trivalent cobalt(III) ion bound to two strongly antiferromagnetically coupled π-radicals. These conclusions agree nicely with Peng's results on the *o*-diiminobenzosemiquinonate (s-bqdi) π-radical complexes $[\mathrm{Co^{III}(s\text{-}bqdi)_2(py)}]\mathrm{Cl}$,[18] $[\mathrm{Co^{III}(s\text{-}bqdi)_2(PPh_3)}](\mathrm{ClO_4})$,[19] and $[\mathrm{Co^{III}Cl(s\text{-}bqdi)_2}]$,[17] all of which were singlet diradicals. These authors were also able to perform the structural characterization of the mononuclear, square-planar species $[\mathrm{Co^{II}(s\text{-}bqdi)_2}]$ ($S = {}^1/_2$),[17] which also contained two *N*,*N*-coordinated *o*-diiminobenzosemiquinonate radicals.

While the occurrence of three different oxidation levels − namely, fully aromatic, semiquinone radical, and quinone forms − has been firmly established in the literature for *o*-catecholates,[20] *o*-phenylenediamines,[21] and *o*-aminophenols,[3−7] this appears not to be the case for *o*-aminothiophenols, for which the occurrence of *o*-iminothiobenzosemiquinonate π-radicals has until very recently been questioned.[1] We have shown for a series of diamagnetic square-planar complexes $[\mathrm{M(L_S^{ISQ})_2}]$ (M = Ni, Pd, Pt)[2] that the semiquinone oxidation level is in fact readily available for *o*-aminothiophenols and we have identified the same structural markers as described above for the *o*-aminophenol derivatives (Scheme 2). *N*,*S*-coordinated *o*-iminothiobenzosemiquinonate radicals possess short C−S bonds, at 1.72−1.74 Å, and short C−N bonds, at 1.35−1.37 Å, and two short C−C and four longer ones (semiquinone sequence). In contrast, in octahedral $[\mathrm{Co^{III}(en)_2(S{-}C_6H_4{-}NH_2)}](\mathrm{ClO_4})\mathrm{Cl}$[22] containing an *N*,*S*-coordinated *o*-aminothiophenolate(1−), the C−S distance is observed to be 1.764(4) Å and the C−N bond length 1.458(4) Å, both of which represent typical single bonds. The six C−C bonds are of equal length, at av. 1.384 Å.

The structure of **2** reveals a nearly ideal square-based pyramidal environment for both cobalt ions in the dinuclear, *S*-bridged neutral molecule ($\mathrm{CoN_2S_3}$). Two *N*,*S*-coordinated, oxidized *o*-aminothiophenolato ligands are in the equatorial plane, and the two imine and the two sulfur donors are each *trans* with respect to each other. One of the two thiolates per cobalt ion forms a bridge with an S-donor in the axial position of the other cobalt ion. The axial Co−S distance in the thiolato bridge [2.351(1) Å] is longer than the corresponding Co−S bond in the equatorial position [2.202(1) Å], and the Co−S bond in the non-bridging thiolate is the shortest at 2.152(1) Å. Thus, the dinuclear molecule in **2** possesses two terminal (nonbridging) *N*,*S*-coordinated ligands and two bridging ligands of this type. Comparison of the dimensions of the non-bridging ligand in **2** with those given in Scheme 2 for an *N*,*S*-coordinated *o*-iminothiobenzosemiquinonate radical immediately implies that this oxidation level is present: the C−S and the C−N bonds are short at 1.720(3) Å and 1.338(4) Å, respectively, and the ring clearly displays quinoid character.

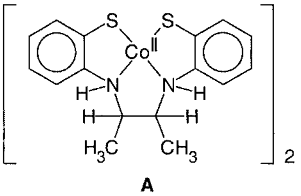
For the bridging ligand, the same oxidation level appears to be appropriate, because the C−N bond is short at 1.348(4) Å and the ring exhibits quinoid character (two shorter C−C bonds and four longer ones). Only the C−S bond at 1.751(3) Å appears to be too long for an *o*-iminothionebenzosemiquinonate radical, but this sulfur atom forms the S-bridge to the second half of the molecule, which may cause the observed lengthening of the C−S bond. We therefore suggest that the molecules in **2** are correctly described as $[Co^{II}(L_S^{ISQ})_2]_2$.

Since we had discovered that **2** displayed valence tautomerism in solution, we also collected an X-ray data set of **2** at 100 K (the above results were obtained from measurements at 295 K). The two structures obtained are identical within experimental error. This is in agreement with the fact that the solid-state electronic spectrum of **2** is temperature-independent in the range 10−300 K.

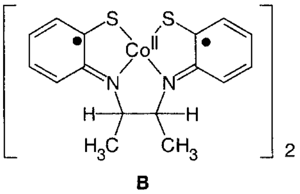
It is interesting that Kawamoto[12] reported the crystal structure of the *monomer* $[Co^{II}(ddbt)]$ ($S = {}^1/_2$), where $(ddbt)^{2-}$ is the diradical-derived from 2,2′-bis(1,2-diphenylenediimine)benzenethiolate. The average C−S bond and C=N bonds here are 1.739(6) and 1.36(1) Å, respectively. The phenyl groups, in a *trans* arrangement relative to one another, effectively prevent dimer formation.

Artaud et al.[11] substituted the two bulky phenyl groups in $[Co^{II}(ddbt)]$ by methyl groups and reported the synthesis of the dinuclear cobalt complexes containing the reduced aromatic *o*-aminothiophenolate ligand (**A**) and its oxidized form (**B**). In contrast to their report, the crystal structure reported is actually that of **B**, since the average C−S and C−N bonds are short at 1.725(6) and 1.35(1) Å, respectively, both rings display quinoid character, and both nitrogen donor atoms are sp^2-hybridized and not sp^3 as required for **A**.

Ref. [11]



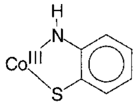
A



B

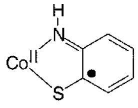
In our view, these authors had not prepared a pure sample of **A**. All the reported spectroscopic and magnetic properties correspond satisfactorily to those of **B** and **2**. In none of the above papers has the ligand diradical character been addressed.

As we have pointed out previously,[2] there are three interesting structures of organometallic cobalt complexes containing either an *N*,*S*-coordinated, aromatic *o*-iminothiophenolate(2−) anion or its one-electron oxidized form *o*-iminothiobenzosemiquinonate(1−). The question, then, is whether we can distinguish between the two forms **C** and **D**.



C

or



D

X-ray structure determinations of $[(tripod)Co(abt)]BF_4$ [23] and $[Co\{P(OCH_3)_3\}_3(abt)]PF_6$ [24] clearly showed that the ligand abt was present as the *o*-iminothiobenzosemiquinonato π-radical, and that both compounds should therefore be viewed as singlet diradicals in which a low-spin Co^{II} ion ($S_{Co} = {}^1/_2$) is antiferromagnetically coupled to an organic π-radical, yielding the observed $S_t = 0$ ground state. The same arguments hold for the neutral complex $Co[\eta^5\text{-}C_5(CH_3)_5][(NH)SC_6H_4]$,[25] in which an *N*,*S*-coordinated *o*-iminothiobenzosemiquinonato radical (and not the reduced aromatic dianion) is also present. It should be noted that *N*,*S*-coordinated dianions $(L_S^{IP})^{2-}$ have the following geometrical features: i) the C−S bond is long at 1.755 Å, as is the C−N bond at 1.40 Å, and ii) the six C−C distances are equal at av. 1.385 Å.

2.3. Electro- and Spectroelectrochemistry

Cyclic voltammograms (CV) of complex **2** were recorded in CH_3CN solutions containing 0.10 M $[nBu_4N]PF_6$ as supporting electrolyte at a glassy carbon working electrode and

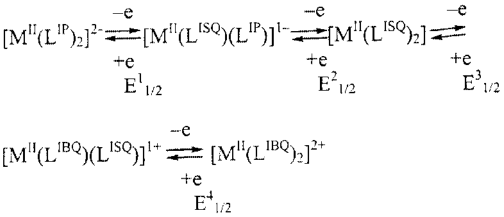
Table 2. Redox potentials in Volts of complexes in CH_2Cl_2 solutions at 20 °C

Complex[a]	$E^1_{1/2}$(2−/1−)	$E^2_{1/2}$(1−/0)	$E^3_{1/2}$(0/1+)	$E^4_{1/2}$(1+/2+)
$[Ni(L_S^{ISQ})_2]$[b]	−1.71	−0.83	0.28	0.90 (irr.)
$[Pd(L_S^{ISQ})_2]$[b]	−1.48	−0.79	0.26	0.83
$[Pt(L_S^{ISQ})_2]$[b]	−1.54	−0.70	0.51	1.20
$[Co(L_S^{ISQ})_2]_2$ [c][d]	−1.90	−0.72	−0.17	+0.4 (irr.)
$[Pd(L_O^{ISQ})_2]$[e]	−1.40	−0.99	0.08	0.47
$[Pt(L_O^{ISQ})_2]$[f]	−1.64	−1.07	0.20	0.70
$[Cu(L_O^{ISQ})_2]$[e]	−1.32	−1.02	−0.26	0.37

[a] Referenced vs. the ferrocenium/ferrocene (Fc^+/Fc) couple; [b] Ref.[2] [c] Measured in CH_3CN. [d] This work. [e] Ref.[4] [f] Ref.[7]

an Ag/AgNO$_3$ reference electrode. Ferrocene was used as an internal standard; all potentials are referenced versus the ferrocenium/ferrocene couple (Fc$^+$/Fc). Table 2 summarizes the results.

Since the original publications by Holm and coworkers[26−27] in the 1970s it has become well established that square-planar complexes of the type [M(L^{ISQ})$_2$] [M = Ni, Pd, Pt; (L^{ISQ})$^{1-}$ represents *o*-iminothiobenzosemiquinonate(1−), *o*-iminobenzosemiquinonate(1−), or *o*-diiminobenzosemiquinonate(1−)] are the central members of a five-membered electron-transfer series, the component species of which (*n* = 2−, 1−, 0, 1+, 2+) are interrelated by reversible one-electron transfer reactions. This has also been shown to be the case for the complexes of Table 2. The reduced and oxidized forms of these neutral species have been shown to contain reduced or oxidized forms of the ligands and a divalent metal center [Equation (5)] by spectroelectrochemical methods.



$$[M^{II}(L^{IP})_2]^{2-} \underset{\substack{+e\\ E^1_{1/2}}}{\overset{-e}{\rightleftharpoons}} [M^{II}(L^{ISQ})(L^{IP})]^{1-} \underset{\substack{+e\\ E^2_{1/2}}}{\overset{-e}{\rightleftharpoons}} [M^{II}(L^{ISQ})_2] \underset{\substack{+e\\ E^3_{1/2}}}{\overset{-e}{\rightleftharpoons}} [M^{II}(L^{IBQ})(L^{ISQ})]^{1+} \underset{\substack{+e\\ E^4_{1/2}}}{\overset{-e}{\rightleftharpoons}} [M^{II}(L^{IBQ})_2]^{2+} \qquad (5)$$

Figure 7 shows the CV of **2** in CH$_3$CN (0.10 M [*n*Bu$_4$N]PF$_6$) at 20 °C over the potential range from +0.6 to −2.1 V vs. Fc$^+$/Fc. Three reversible electron-transfer waves were observed, at −1.90, −0.72, and −0.17 V, each wave corresponding to a one-electron transfer event per cobalt ion present, as established by coulometry. Since we have established that **2** is a dimer in the solid state, we briefly studied its solution behavior. A frozen CH$_2$Cl$_2$ solution of **2** at 10 K displayed a weak X-band EPR spectrum at $g \approx 2.0$ typical for the $S = {}^1/_2$ monomeric species [Co^{II}(L$_S^{ISQ}$)$_2$]. Hence, the equilibrium Equation (6) exists in solution, and both the dissociation and formation rates of this equilibrium are expected to be very fast with respect to the scan rates employed in the cyclic voltammetry experiments. From the results described below we inferred that the monomers were the electroactive species.

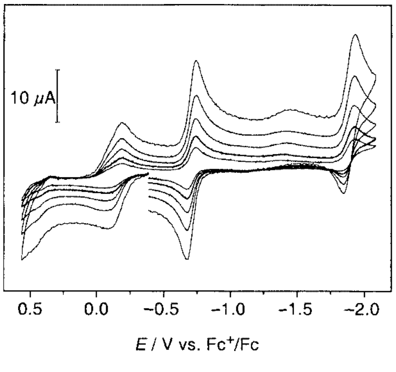
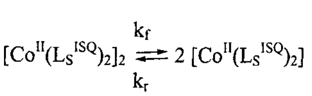


Figure 7. Cyclic voltammogram of **2** in CH$_3$CN solution (0.10 M [*n*Bu$_4$N]PF$_6$) at 20 °C at a glassy carbon working electrode; scan rates: 50, 100, 200, 400, 500 mV s^{-1}



$$[Co^{II}(L_S^{ISQ})_2]_2 \underset{k_r}{\overset{k_f}{\rightleftharpoons}} 2\,[Co^{II}(L_S^{ISQ})_2] \qquad (6)$$

Coulometric measurements established that the monomer of **2** could be reduced in a one-electron fashion at a fixed potential of −1.0 V and by another electron at −2.0 V, and oxidized by 1 e$^-$ at 0.15 V. Thus a monocation, a monoanion, and a dianion can be reversibly generated from **2** electrochemically. The dianion proved to be too sensitive for further investigation. Figure 8 shows the electronic spectra of **2** and of its electrochemically generated monocation and monoanion in CH$_3$CN; Table 3 summarizes these results.

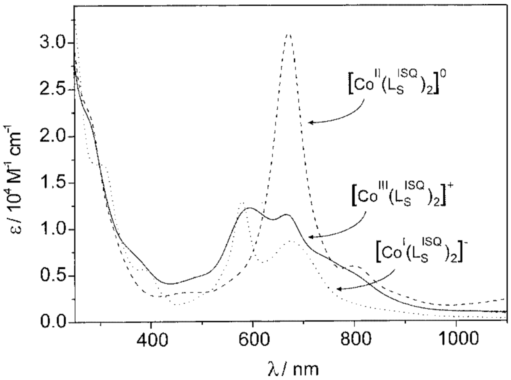


Figure 8. Electronic spectra of **2** and of its electrochemically generated monocation and monoanion in CH$_3$CN solution (0.10 M [*n*Bu$_4$N]PF$_6$) at 20 °C

Table 3. Electronic spectra of complexes in CH$_2$Cl$_2$ solution

Complex	λ_{max} [nm] (10^4 ε [M^{-1} cm^{-1}])[a]
1	375 sh (0.4), 446 (0.42), 514 sh (0.16)
2 (H)[b]	279 sh (1.8), 458 sh (0.25), 554 sh (0.5), 678 (2.9), 806 (0.60), 901 sh (0.2), 1150 (0.6)
L[c]	611 (1.0), 712 (0.96), 885 (0.60)
[Co^I(L$_S^{ISQ}$)$_2$]$^{1-}$ [d]	311 sh (1.7), 398 sh (0.52), 589 (1.3), 681 (0.80), 810 sh (0.5)
[Co^{III}(L$_S^{ISQ}$)$_2$]$^{1+}$ [d]	283 sh (2.2), 380 sh (0.75), 594 (1.3), 671 (1.2), 813 sh (0.6)
3	390 (0.7), 500 sh (0.7), 600 sh (1.55), 640 (1.7), 770 (0.9)
4	283 (2.3), 434 (0.6), 566 (0.78), 695 (1.9), 884 (1.0)
5	277 (2.3), 672 (1.5), 821 (1.3)

[a] Molar absorption coefficients are given *per cobalt ion* (monomer). [b] High-temerature spectrum (20 °C). [c] Low-temperature spectrum (−70 °C). [d] Electrochemically generated in CH$_3$CN (0.10 M [*n*Bu$_4$N]PF$_6$).

Rather surprisingly, the spectra both of the monocation and of the monoanion of **2** did not resemble those reported[2] for [M^{II}(L$_S^{IBQ}$)(L$_S^{ISQ}$)]$^+$ and [M^{II}(L$_S^{IP}$)(L$_S^{ISQ}$)]$^-$ (M = Ni, Pt), respectively. We therefore concluded that a distribution of ligand and metal oxidation levels as in these cases did not prevail for the oxidized and reduced forms of

2. In fact, it was rather remarkable that the spectra of these two species were fairly similar, both displaying two prominent absorption maxima in the visible region, at ca. 590 and 675 nm ($\varepsilon \approx 10^4$ M^{-1} cm^{-1}). Furthermore, these spectra resembled that of $[Co^{III}(L_S^{ISQ})_2I]$ (**3**), shown in Figure 3. We therefore suggest that neither the oxidation of **2** nor its reduction was ligand-centered. Instead, the spectra imply the presence of two $(L_S^{ISQ})^{1-}$ π-radical ligands and metal-centered redox activity [Equation (7)].

$$\begin{array}{ccccc} [Co^{III}(L_S^{ISQ})_2]^+ & \underset{-e}{\overset{+e}{\rightleftharpoons}} & [Co^{II}(L_S^{ISQ})_2]^0 & \underset{-e}{\overset{+e}{\rightleftharpoons}} & [Co^{I}(L_S^{ISQ})_2] \\ S = 0 & & S = {}^1/_2 & & S = 0 \\ & E^3_{1/2} & & E^2_{1/2} & \end{array} \qquad (7)$$

Note that the electronic spectrum of the valence tautomer of **2** (see above), namely $[Co^{III}(L_S^{IP})(L_S^{ISQ})]_2$, was significantly different from those reported here for the monocation and -anion, but that it did closely resemble those reported for $[Ni^{II}(L_S^{IP})(L_S^{ISQ})]^-$ and $[Pt(L_S^{IP})(L_S^{ISQ})]^-$, both of which displayed three absorption maxima, at 650, 840, 971 nm for the Ni complex and at 850, 916, 980 nm for the Pt analogue.[2] In $[Co^{III}(L_S^{IP})(L_S^{ISQ})]_2$ these bands were shifted to higher energies (611, 712, 885 nm). It is also remarkable that the electronic spectra of **4** and **5** (Figure 6) were also very similar to those of $[Co^{III}(L_S^{ISQ})_2]^+$ and $[Co^{I}(L_S^{ISQ})_2]^-$.

We would like to stress that the assignments of oxidation levels of the metal ions and the ligands for the monoanion of **2** and its monocationic form are tentative at present; they are based only on the similarity of their electronic spectra. Further investigations of these species are clearly necessary.

Experimental Section

Syntheses: The ligands 2-anilino-4,6-di-*tert*-butylphenol ($H[L_O^{AP}]$) and 6-amino-2,4-di-*tert*-butylthiophenol ($H[L_S^{AP}]$) were prepared according to published procedures.[4,8]

$[Co^{II}(L_S^{AP})_2]_2 \cdot 2CH_3CN$ (1·2CH$_3$CN): A degassed solution of the ligand $H[L_S^{AP}]$ (0.50 g, 2.0 mmol) and $CoCl_2$ (0.13 g, 1.0 mmol) in dry acetonitrile (40 mL) was stirred under strictly anaerobic conditions (under Ar) for 10 min at ambient temperature. Triethylamine (0.20 g, 2.0 mmol) was added dropwise to the filtered green solution, and stirring was continued for 40 min. A microcrystalline solid precipitated from the light orange solution and was collected by filtration. The material was extremely air-sensitive and had to be stored under argon. Yield: 0.39 g (73% with respect to Co). $C_{56}H_{88}Co_2N_4S_4 \cdot 2CH_3CN$ (1143.55): calcd. C 62.93, H 8.28, Co 10.31, N 7.34; found C 62.7, H 8.4, Co 10.5, N 7.2. IR (KBr disk): $\tilde{\nu}$ = 3322, 3268, 3246 [ν(NH$_2$)] cm^{-1}.

$[Co^{II}(L_S^{ISQ})_2]_2 \cdot n$-Hexane (2·*n*-Hexane): When a solid sample of **1**·2CH$_3$CN (0.39 g) was exposed to air, the orange microcrystals immediately turned black. Some of this black material (0.20 g) was dissolved in CH_2Cl_2 (40 mL) under argon. *n*-Hexane (20 mL) was added to the blue solution, and the solvents were allowed to evaporate slowly. Black crystals of **2**·*n*-hexane (0.17 g, 73%) were obtained. Single crystals of this material were grown from a benzene/*n*-hexane mixture (1:1) under argon by slow evaporation. $C_{56}H_{84}Co_2N_4S_4 \cdot C_6H_{14}$ (1145.61): calcd. C 65.00, H 8.62, N 4.89; found C 64.8, H 8.7, N 5.0. MS (ESI$^+$): *m*/*z* = 1059 [M$^+$]. IR (KBr disk): $\tilde{\nu}$ = 3296 [ν(N−H)] cm^{-1}.

$[Co^{III}I(L_S^{ISQ})_2]$ (3): A solution of iodine (0.05 g, 0.20 mmol) in *n*-hexane (25 mL) was added dropwise with stirring under argon to a solution of **2**·*n*-hexane (0.225 g, 0.20 mmol) in CH_2Cl_2 (40 mL). The blue color of the solution changed to dark green. After the mixture was stirred for 15 min at 20 °C, the solvents were evaporated under reduced pressure. *n*-Hexane (20 mL) was added to the dark residue. A dark green residue was filtered off. This material was recrystallized from a mixture of CH_2Cl_2 (40 mL) and CH_3CN (25 mL) (which were allowed to slowly evaporate) in an argon stream. Yield: 0.17 g (68% based on **2**). $C_{28}H_{42}CoIN_2S_2$ (656.62): calcd. C 51.22, H 6.45, Co 8.98, I 19.33, N 4.27, S 9.77; found C 51.4, H 6.5, Co 9.2, I 18.9, N 4.2, S 10.2. MS (EI): *m*/*z* = 529 [M$^+$ − I]. ^1H NMR (250 MHz, CDCl$_3$, 300 K): δ = 1.73 (s, 18 H), 1.33 (s, 18 H), 7.67 (br, 2 H), 7.85 (br, 2 H), 12.85 (br, 2 H, N−H) ppm. IR (KBr disk): $\tilde{\nu}$ = 3231 [ν(N−H)] cm^{-1}.

$[Co^{III}I(L_O^{ISQ})_2]$ (4): Triethylamine (0.3 mL) was added to a solution of the ligand $H[L_O^{AP}]$ (0.30 g, 1.0 mmol) and CoI_2 (0.20 g, 0.64 mmol) in CH_3CN (25 mL). The solution was stirred in the presence of air at 20 °C for 30 min and filtered. A black precipitate formed upon standing for 12 h at ambient temperature, and was collected by filtration. Yield: 0.17 g (43% based on $H[L_O^{AP}]$). Single crystals suitable for X-ray crystallography were grown from a methanol/chloroform solution (1:2) of the above black material. $C_{40}H_{50}CoIN_2O_2$ (776.69): calcd. C 61.80, H 6.49, N 3.61; found C 62.0, H 6.5, N 3.5. MS (EI): *m*/*z* = 776 [M$^+$], 649 [M$^+$ − I]. ^1H NMR (400 MHz, CDCl$_3$, 300 K): δ = 8.78 (t, 2 H), 7.90 (s, 2 H), 7.57 (t, 4 H), 7.42 (s, 2 H), 7.31 (d, 4 H), 1.53 (s, 18 H), 1.10 (s, 18 H).

$[Co^{III}Cl(L_O^{ISQ})_2]$ (5): A solution of triethylamine (0.6 mL) in CH_3CN (10 mL) was added to a solution of $[Co(H_2O)_6](BF_4)_2$ (0.68 g, 2.0 mmol) and the ligand $H[L_O^{AP}]$ (0.60 g, 2.0 mmol) in CH_3CN (30 mL). The mixture was stirred in the presence of air at room temperature for 2 h and filtered. The solvent was allowed to evaporate, yielding a dark solid residue that was recrystallized from a $CH_3CN/CHCl_3$ (1:1) mixture to give a small amount (ca. 10%) of crystalline **5**. The Cl$^-$ ligand in **5** is believed to be abstracted from the CHCl$_3$ solvent. $C_{40}H_{50}ClCoN_2O_2$ (685.24): calcd. C 70.11, H 7.35, N 4.09; found C 70.2, H 7.3, N 4.0. MS (ESI$^+$): *m*/*z* = 684 [M$^+$]; 649 [M − Cl$^+$].

X-ray Crystallographic Data Collection and Refinement of the Structures: Dark red-brown single crystals of **2**, and black crystals of **4** and **5**, were coated with perfluoropolyether. Suitable crystals were picked up with a glass fiber and were immediately mounted in the nitrogen cold stream of the diffractometers to prevent loss of solvent. Intensity data were collected at 100 K with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å); a second crystal of **2** was measured at 293(2) K. Final cell constants were obtained from a least-squares fit of a subset of several thousand strong reflections. Data collection was performed by hemisphere runs, taking frames at 0.3° (Siemens SMART) and 1.0° (Nonius Kappa-CCD) in ω. A semiempirical absorption correction was performed on the low-temperature data set of **2** by use of the program SADABS.[28] Intensity data of **2** measured at room temperature, **4**, and **5** were corrected with the Gaussian-type face-indexed absorption correction routine embedded in XPREP.[29] The ShelXTL[29] software package was used for solution, refinement, and depiction of the

Table 4. Crystallographic data for **2**·0.5hexane (293 K), **2**·hexane (100 K), **4**, and **5**

	2·0.5 hexane	**2**·hexane	**4**	**5**
Empirical formula	$C_{59}H_{91}Co_2N_4S_4$	$C_{62}H_{98}Co_2N_4S_4$	$C_{40}H_{50}CoIN_2O_2$	$C_{40}H_{50}ClCoN_2O_2$
Formula mass	1102.46	1145.54	776.65	685.20
Space group	$P\bar{1}$, no. 2	$P\bar{1}$, no. 2	$P2_1/c$, no. 14	$Pca2_1$, no. 29
a [Å]	10.5636(9)	10.496(2)	13.5489(9)	26.888(2)
b [Å]	11.4954(12)	11.145(2)	26.290(2)	12.6938(10)
c [Å]	14.5182(12)	14.513(3)	11.6662(8)	10.9282(8)
α [°]	103.73(1)	101.02(2)	90	90
β [°]	101.85(1)	103.66(2)	113.31(1)	90
γ [°]	99.13(1)	99.23(2)	90	90
V [Å]	1635.7(3)	1581.2(5)	3816.3(5)	3729.9(5)
Z	1	1	4	4
T [K]	293(2)	100(2)	100(2)	100(2)
ρ(calcd.) [g cm^{-3}]	1.119	1.203	1.352	1.220
Diffractometer used	Nonius Kappa-CCD	Siemens SMART	Siemens SMART	Siemens SMART
Refl. collected/Θ_{max}	13372/54.00	6152/46.54	33336/54.98	31976/55.00
Unique refl./$I > 2\sigma(I)$	6949/5355	4140/2730	8726/6854	6813/5395
No. of params/restraints	337/4	331/1	427/0	415/1
μ(Mo-K_α) [cm^{-1}]	6.70	6.96	12.93	5.67
$R1^{[a]}$/goodness of fit$^{[b]}$	0.0546/1.043	0.0601/0.845	0.0329/1.027	0.0548/1.026
$wR2^{[c]}$ ($I > 2\sigma(I)$]	0.1429	0.1367	0.0655	0.1268

[a] Observation criterion: $I > 2\sigma(I)$. $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] GooF = $\{\Sigma[w(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$. [c] $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$ where $w = 1/\sigma^2(F_o^2) + (aP)^2 + bP$, $P = (F_o^2 + 2F_c^2)/3$.

structure. The structures were readily solved by Patterson methods and difference Fourier techniques. The hexane solvent molecule in the room-temperature structure of **2** was found to be disordered and not fully occupied. A split-atom model with restrained C−C distances and a reduced occupation factor satisfactorily described the disorder. All non-hydrogen atoms, except C atoms in disordered parts, were refined anisotropically and hydrogen atoms were placed at calculated positions and refined as riding atoms with isotropic displacement parameters. Crystallographic data of the compounds and diffractometer types used are listed in Table 4. CCDC-178090−178093 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Physical Measurements: Electronic spectra of complexes and spectra of the spectroelectrochemical measurements were recorded with an HP 8452A diode array spectrophotometer (range: 190−1100 nm). Cyclic and square-wave voltammograms and coulometric experiments were performed with an EG&G potentiostat/galvanostat. Temperature-dependent (2−298 K) magnetization data were recorded with a SQUID magnetometer (MPMS Quantum design) in an external magnetic field of 1.0 T. The experimental susceptibility data were corrected for underlying diamagnetism by use of tabulated Pascal's constants. X-band EPR spectra were recorded with a Bruker ESP 300 spectrometer.

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