Spin-Crossover Complexes

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Temperature-Induced Spin-Transition in a Low-Spin Cobalt(II) Semiquinonate Complex**

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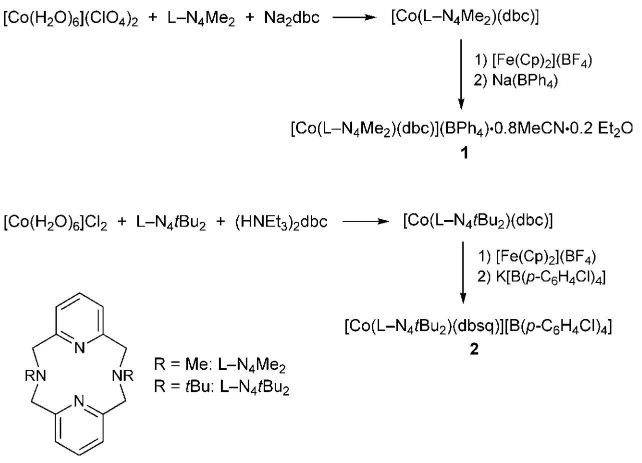
Dedicated to Professor Christoph Elschenbroich on the occasion of his 70th birthday

Spin crossover and valence tautomerism are examples of processes that can be utilized as a basis for achieving molecular switches.[1] Whereas the spin-crossover process is characterized by a temperature-, pressure-, or light-induced change of the electronic state of the metal ion to one with a different spin multiplicity,[2] valence tautomerism entails an intramolecular redox reaction between a metal ion and a coordinated ligand, which, in a few instances, is accompanied by a change in the spin state of the metal ion.[3] Various reported low-spin cobalt(III) catecholate complexes, which can be transformed into high-spin cobalt(II) semiquinonate complexes by raising the temperature, provide excellent examples of the latter process. In contrast, spin-crossover chemistry is dominated by octahedral iron(II) complexes with a FeN_6 coordination sphere;[2] however, there are only very few known octahedral cobalt(II)-containing spin-crossover complexes.[4] Herein we describe the first cobalt(II) semiquinonate complex that displays spin-crossover properties rather than valence tautomerism.



Scheme 1. Preparation of compounds **1** and **2**.

The starting point of our investigation was the olive-green cobalt(III) 3,5-di-*tert*-butylcatecholate (dbc^{2-}) complex [Co(L-N_4Me_2)(dbc)](BPh_4)·0.8 MeCN·0.2 Et_2O (**1**) containing the dimethyl derivative of the tetraazamacrocyclic ligand 2,11-diaza[3.3](2,6)pyridinophane (L-N_4Me_2) as coligand. This complex was obtained in 42% yield by oxidation of the red cobalt(II) catecholate complex [Co(L-N_4Me_2)(dbc)] (prepared in situ from equimolar solutions of cobalt(II) perchlorate, L-N_4Me_2, and 3,5-di-*tert*-butylcatecholate) with ferrocenium tetrafluoroborate ($[Fe(Cp)_2](BF_4)$; Cp = cyclopentadienyl), followed by a metathesis reaction with sodium tetraphenylborate (Scheme 1). In accordance with the description of **1** as a cobalt(III) catecholate complex, solutions and solids of this substance are diamagnetic. X-ray structure analysis of **1** also supports this assignment.[6] Figure 1 shows a perspective view of the complex cation in **1**. Because of the small size of the macrocyclic ring, the coordinated ligand L-N_4Me_2 is folded along the N_{amine}–N_{amine} axis, thereby rendering a distorted *cis*-octahedral coordina-

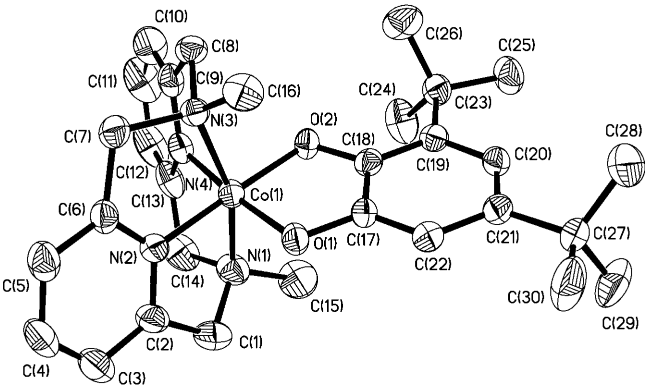


Figure 1. Perspective view of the complex cation in **1** showing 50% thermal ellipsoids; selected bond lengths [Å]: Co(1)–N(1) 1.978(3), Co(1)–N(2) 1.853(2), Co(1)–N(3) 1.980(2), Co(1)–N(4) 1.843(2), Co(1)–O(1) 1.856(2), Co(1)–O(2) 1.865(2), C(17)–O(1) 1.362(3), C(18)–O(2) 1.359(3).

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Supporting information (synthetic procedures and characterization data of complexes **1** and **2**) for this article is available on the WWW under http://dx.doi.org/10.1002/anie.200903789.

tion environment. Thus, the cobalt ion is coordinated to the two oxygen donor atoms of the catecholate moiety and the two pyridine nitrogen donor atoms of the tetraazamacrocyclic ligand in the equatorial plane, and to the two amine nitrogen donor atoms in the axial positions. In all *cis*-octahedral transition-metal complexes containing L-N_4Me_2 as ligand, the axial metal–N_{amine} bonds are longer than the equatorial metal–N_{py} bonds by at least 0.1 Å.[7] In addition, the lengths of the bonds between the metal ion and the nitrogen atoms of the tetraazamacrocyclic ligand are quite characteristic of the respective spin state and oxidation state of the coordinated metal ion; they can, therefore, be used as diagnostic tools for determining the electronic state of the metal ion. Thus, the observation of rather short Co–N_{py} and Co–N_{amine} bond lengths of (1.848 ± 0.005) Å[8] and (1.979 ± 0.001) Å, respectively, is consistent only with the presence of a low-spin cobalt(III) ion. Further, the average of the C–O bond lengths of (1.361 ± 0.002) Å as well as the more or less equal C–C bond lengths within the aromatic ring clearly identify the coordinated dioxolene ligand as a catecholate unit.[3c,9] This electronic ground state prevails even at higher temperatures.

To be able to reach the cobalt(II) electronic state by raising the temperature, the capability of the ligand to donate electron density to the metal ion has to be reduced. By introducing bulky amine substituents such as *tert*-butyl groups into the macrocyclic ligand, this objective can be accomplished because the amine substituents of the coordinated tetraazamacrocycle are located above and below the two *cis*-oriented coordination sites of the dioxolene ligand, and, therefore, the larger steric interactions between the *tert*-butyl groups and the dioxolene ligand will increase the Co–N_{amine} bond length. Thereby, the capability of the ligand to donate electron density to the coordinated metal ion is weakened and at the same time the ligand-field strength of the di-*tert*-butyl-substituted macrocycle L-$N_4t$$Bu_2$ is reduced relative to that of the ligand L-N_4Me_2.

Employing an analogous synthetic procedure as before, but starting with L-$N_4t$$Bu_2$ instead of L-N_4Me_2 and using potassium tetra(*p*-chlorophenyl)borate in the metathesis reaction afforded the analytically pure, dark green compound [Co(L-$N_4t$$Bu_2$)(dbsq)](B(*p*-$C_6H_4Cl$)$_4$) (**2**) in 61% yield ($dbsq^-$ = 3,5-di-*tert*-butylsemiquinonate; Scheme 1) The biggest difference between the UV/Vis spectra of **1** and **2** is the presence of an intense CT absorption band with a maximum at 1075 nm ($\varepsilon_M = 7640\,L\,mol^{-1}\,cm^{-1}$) and a shoulder at 1042 nm ($\varepsilon_M = 6890\,L\,mol^{-1}\,cm^{-1}$) for **2** (Figure 2). This observation as well as the paramagnetism of **2** in solution (as evidenced by its NMR spectrum) point towards a different electronic ground state of **2** compared to that of **1**. The structure of **2** was determined at 100 K (Figure 3).[10] As expected of a low-spin d^7 metal ion, the Jahn–Teller effect places the unpaired electron in the σ-antibonding d_{z^2} orbital, whereas in the high-spin state both σ-antibonding d orbitals are singly occupied. Therefore, in cobalt(II) complexes containing the macrocyclic ligand L-$N_4t$$Bu_2$, the Co–$N_{amine}$ bonds are quite elongated in both the high-spin (2.351–2.460 Å) and the low-spin complexes (2.368–2.404 Å), whereas the Co–N_{py} bond lengths differ considerably between low-spin (1.902–1.940 Å) and high-spin complexes (2.082–2.096 Å).[11] In the structure of **2**, the averages of the Co–N_{py} and the Co–N_{amine} bond lengths of (1.932 ± 0.001) Å and (2.338 ± 0.030) Å,[12] respectively, indicate a low-spin cobalt(II) ion. In addition, the average of the C–O bond lengths of (1.313 ± 0.002) Å falls into the range commonly observed for coordinated semiquinonate radicals. In contrast to **1**, inspection of the C–C bonds in **2** reveals a more localized π-bonding pattern of an *ortho*-semiquinonate radical with short bonds between the carbon atoms C(25) and C(26) as well as between C(27) and C(28), and a rather long bond between the carbon atoms C(23) and C(24).[3a,9] On the basis of these results, we conclude that, at 100 K, complex **2** can be adequately described as a low-spin cobalt(II) semiquinonate complex.

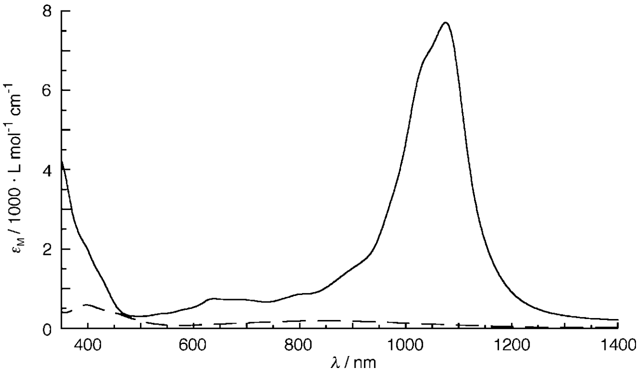

Figure 2. Electronic absorption spectra of **1** (dashed line) and **2** (solid line) in acetonitrile.

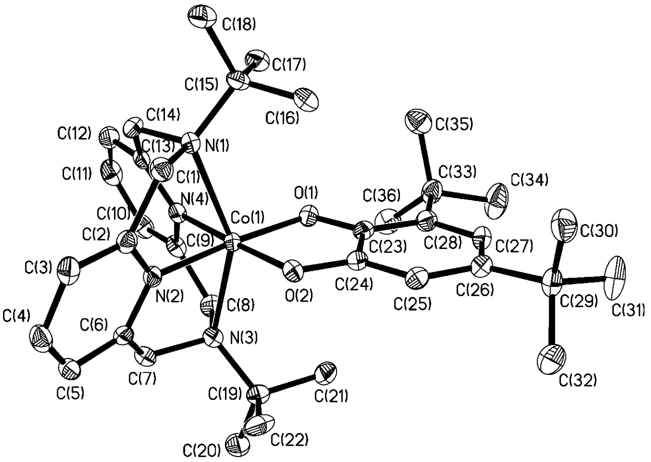

Figure 3. Perspective view of the complex cation in **2** showing 50% thermal ellipsoids; selected bond lengths [Å] at 100 K [at 400 K]: Co(1)–N(1) 2.308(2) [2.320(3)], Co(1)–N(2) 1.932(2) [1.994(3)], Co(1)–N(3) 2.368(2) [2.371(3)], Co(1)–N(4) 1.931(2) [1.987(3)], Co(1)–O(1) 1.888(1) [1.974(2)], Co(1)–O(2) 1.892(1) [1.964(2)], C(23)–O(1) 1.311(2) [1.307(4)], C(24)–O(2) 1.315(3) [1.274(4)].

The magnetic properties of compound **2** were investigated over a temperature range from 2 to 400 K with a SQUID magnetometer. The dependence of $\chi_M T$ versus T is depicted in Figure 4. The graph can be divided into three parts: Between 40 and 200 K, the curve reaches a plateau with a

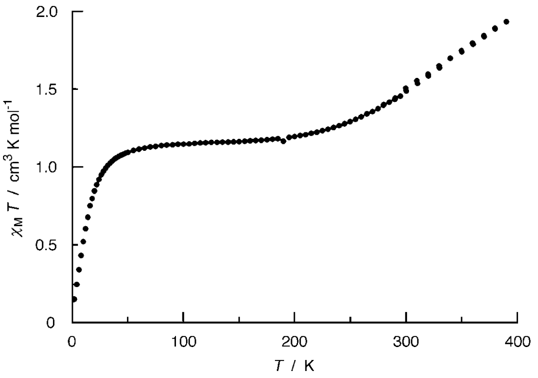

Figure 4. Variation of the product $\chi_M T$ with temperature for solid **2** at an applied magnetic field of 0.5 T.

value for $\chi_M T$ of about 1.16 cm^3 K mol^{-1}. This value corresponds to a species with a spin state of $S=1$. Taking the assignment of **2** as a low-spin cobalt(II) semiquinonate complex as the basis for describing the electronic ground state, one unpaired electron resides in the σ-antibonding d_{z^2} orbital, the other unpaired electron occupies a π-molecular orbital of the semiquinonate radical. Considering that both orbitals are orthogonal to each other and based on related complexes with copper(II) ions,[13] a strong ferromagnetic exchange coupling between both spin carriers is expected. The observance of a ground state of $S=1$ is, therefore, consistent with the interpretation of the structural data at 100 K. Below 40 K, the $\chi_M T$ curve falls to a value of 0.15 cm^3 K mol^{-1}. This behavior can be attributed to zero-field splitting and/or to very weak intermolecular antiferromagnetic coupling within the crystal lattice. A similar decrease was found in copper(II) semiquinonate complexes with the same spin ground state.[13b] However, the most remarkable finding is that, above 200 K, there is a steady increase of the $\chi_M T$ curve to about 1.98 cm^3 K mol^{-1} at 400 K. This finding can only be attributed to a gradually occurring spin transition from a low-spin to a high-spin cobalt(II) state. This spin-crossover process is, however, not complete at 400 K. In reported high-spin cobalt(II) semiquinonate complexes, the exchange coupling between the $S=3/2$ spin of the high-spin cobalt(II) ion and the $S=1/2$ spin of the semiquinonate radical is generally described as antiferromagnetic, leading to a spin ground state of $S=1$ with a moderate coupling constant.[3,14] Any fitting of the magnetic data to a theoretical model is problematic because both the spin transition process and the exchange coupling contribute to the values of the $\chi_M T$ curve above 200 K, no data are available to us above 400 K (the high-temperature limit of the SQUID magnetometer), and the removal of degeneracy of the $^4T_{1g}$ state in a high-spin octahedral cobalt(II) ion as a result of distortion of the ligand field and spin–orbit coupling can complicate a magnetic analysis even without the occurrence of spin crossover.[14] We felt that any attempt to simulate the powder susceptibility data including all those effects would suffer from severe overparametrization. Hence, no unambiguous and reliable values for the exchange coupling constant and the critical spin-crossover temperature can be derived at this time.

To prove that a spin transition is indeed responsible for the increase of the $\chi_M T$ value above 200 K, data collection for a structure analysis was carried out at 400 K. The results of this structural investigation demonstrate that the axial Co–N_{amine} bond lengths remain nearly the same, whereas the equatorial Co–N_{py} and Co–O bond lengths significantly increase with temperature. Thus, the averages of the Co–N_{py} and of the Co–O bond lengths change from (1.931 ± 0.001) Å to (1.991 ± 0.004) Å and from (1.890 ± 0.002) Å to (1.969 ± 0.005) Å, respectively. The observed Co–N_{py} bond lengths at 400 K indicate, too, that the spin transition is not complete at this temperature.[11] The slightly decreased C–O bond lengths at 400 K are still in the range of those in coordinated semiquinonate radicals, but an increasing asymmetry between both C–O bonds is discernible.[3c,9]

In summary, magnetic as well as structural data unequivocally demonstrate that a temperature-induced spin-crossover process takes place in complex **2**. Spin-crossover complexes with cobalt(II) ions are still considered rare and are generally only observed with strong-field ligands. Further, to best of our knowledge, until now temperature-induced changes of the spin state in cobalt dioxolene complexes have all been linked to valence tautomerism. Therefore, complex **2** is the first known low-spin cobalt(II) semiquinonate complex and also the first known cobalt dioxolene complex that undergoes temperature-induced spin changes as a result of spin crossover rather than valence tautomerism.

We attribute this finding to the special structural features of the coordinated ligand L-N_4tBu$_2$. In combination with a semiquinonate ligand, this macrocyclic ligand still exerts sufficient ligand-field strength to enforce a low-spin state as the ground state upon the cobalt(II) ion. Because of the steric interactions between the *tert*-butyl substituents and the ligand at the two *cis*-oriented coordination sites, the axial Co–N_{amine} bonds are considerably elongated. In a low-spin cobalt(III) complex containing L-N_4tBu$_2$, the axial Co–N_{amine} bond lengths were found to be approximately 2.09 Å.[15] Thus, Co^{III}–N_{amine} bonds are about 0.1 Å longer in low-spin cobalt(III) complexes containing L-N_4tBu$_2$ than in those containing L-N_4Me$_2$. In the low-spin cobalt(II) complex, the prevailing Jahn–Teller effect favors the long axial Co–N_{amine} bonds, which are also enforced by the macrocyclic ligand L-N_4tBu$_2$. Upon oxidizing the cobalt(II) ion to a cobalt(III) ion, the anticipated decrease of the Co–N_{amine} bond lengths results in stronger steric interactions between the *tert*-butyl substituents and the dioxolene ligand. All of these factors destabilize the cobalt(III) state relative to the cobalt(II) state in complexes that contain the macrocycle L-N_4tBu$_2$. Consequently, this increase in the redox potential of the [Co(L-N_4tBu$_2$)]$^{2+/3+}$ fragment relative to that of the coordinated dioxolene ligand is responsible for the presence of the low-spin cobalt(II) semiquinonate ground state in **2**.

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[5] The presence of nonstoichiometric amounts of MeCN and Et_2O in compound **1** is based on the X-ray structure determination, NMR spectroscopic results, and chemical analysis. The content can vary depending of the method used for quantification, rendering a general formulation of **1** as $[Co(L\text{-}N_4Me_2)(dbc)](BPh_4)\cdot(MeCN)_x\cdot(Et_2O)_{1-x}$ ($x = 0.7$–0.9). We assumed an averaged composition of the formulation as $[Co(L\text{-}N_4Me_2)(dbc)](BPh_4)\cdot 0.8\,MeCN\cdot 0.2\,Et_2O$, which imposes a maximum error of less than 0.5% on calculations concerning molar amounts.

[6] Crystal data for **1**: $C_{54}H_{60}BCoN_4O_2$, $M_r = 866.80$, monoclinic, space group $P2_1/n$, $a = 19.020(2)$, $b = 13.889(1)$, $c = 21.177(2)$ Å, $\beta = 110.98(1)°$, $V = 5223(1)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.102\ g\,cm^{-3}$; $T = 193$ K, $\mu(Mo_{K\alpha})$ 0.369 mm^{-1} ($\lambda = 0.71073$ Å); 55758 reflections measured, 10900 unique, refinement converged to $R = 0.0455$, $wR^2 = 0.0779$ ($I > 2\sigma(I)$), 567 parameters and 0 restraints. Disordered solvent molecules (MeCN and Et_2O) were found within an area of a packing gap ($x = 0.56$, $y = 0.60$, $z = 0.61$). A definite determination of the only partially occupied positions was not possible. Therefore, a modified set of reflection data was calculated with the option SQUEEZE of the program PLATON so that the contribution to the reflection data from this area of the packing gap is not included in the refinements. Min./max. residual electron density $= +0.266/-0.279$ e Å^{-3}. CCDC 748989 (**1**), 748991 (**2**, 100 K),[10] and 748990 (**2**, 400 K)[10] 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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[10] Crystal data for **2**: a) at 100 K: $C_{60}H_{68}BCl_4CoN_4O_2$, $M_r = 1088.72$, monoclinic, space group $P2_1/n$, $a = 10.3507(1)$, $b = 26.2575(2)$, $c = 20.5763(2)$ Å, $\beta = 101.778(1)°$, $V = 5474.6(1)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.321\ g\,cm^{-3}$; $T = 100$ K, $\mu(Cu_{K\alpha}) = 4.613$ mm^{-1} ($\lambda = 1.5418$ Å); 30291 reflections measured, 8658 unique, refinement converged to $R = 0.0340$, $wR^2 = 0.0821$ ($I > 2\sigma(I)$), 661 parameters and 0 restraints; min./max. residual electron density $= +0.284/-0.357$ e Å^{-3}; b) at 400 K: $a = 10.478(1)$, $b = 26.873(1)$, $c = 20.977(1)$ Å, $\beta = 102.93(1)°$, $V = 5757(1)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.256\ g\,cm^{-3}$; $T = 400$ K, $\mu(Mo_{K\alpha})$ 0.528 mm^{-1} ($\lambda = 0.71073$ Å); 35029 reflections measured, 11621 unique, refinement converged to $R = 0.0530$, $wR^2 = 0.0689$ ($I > 2\sigma(I)$), 661 parameters and 0 restraints; min./max. residual electron density $= +0.236/-0.208$ e Å^{-3}.

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[12] In many octahedral metal complexes containing $L\text{-}N_4tBu_2$ as coligand, the two axial $M{-}N_{amine}$ bonds differ substantially in length. This result also explains the rather large range of values found for $Co{-}N_{amine}$ bond lengths in complexes of this type.

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[15] The cobalt(III) complex $[Co(L\text{-}N_4tBu_2)(NSC)_2](BF_4)\cdot EtCN$ was prepared and characterized by X-ray crystallography. The averages of the $Co{-}N_{py}$ and of the $Co{-}N_{amine}$ bond lengths in this complex are 1.876 and 2.093 Å, respectively. Interestingly, in contrast to the cobalt(II) complexes, the lengths of both $Co{-}N_{amine}$ bonds differ only by 0.003 Å. S. Reh, H. Kelm, H.-J. Krüger, unpublished results.