Notes

Redox-Tunable Valence Tautomerism in a Cobalt Schiff Base Complex

Daniel Ruiz-Molina,[1a] Jaume Veciana,[1a]
Klaus Wurst,[1b] David N. Hendrickson,*[,1c] and
Concepció Rovira*[,1a]

Institut de Ciència de Materials de Barcelona (CSIC),
Campus Universitari de Bellaterra, 08193 Cerdanyola, Spain,
Institut für Allgemeine, Anorganische und Teoretische
Chemie, Universität Innsbruck, Innrain 52a,
A-6020 Innsbruck, Austria, and University of California at
San Diego, La Jolla, California 92093-0358

Received June 17, 1999

Introduction

Cobalt complexes with redox-active ligands that interconvert between two stable states in response to external stimuli have been proposed as potential building blocks to obtain molecular switching devices, where the ultimate goal is to manipulate information at the molecular level.[2,3] Cobalt *o*-quinone complexes have two valence tautomeric isomers with different net magnetic moments and optical properties: the low-spin (*ls*) [Co^{III}(N-N)(DBSQ)(DBCat)] and the high-spin (*hs*) [Co^{II}(N-N)(DBSQ)$_2$] where N-N is a bidentate nitrogen ligand and DBSQ$^-$ and DBCat^{2-}, respectively, are the semiquinonate and catecholate forms of 3,5-di-*tert*-butyl-1,2-benzoquinone (DBQ).[4,5] Both isomers can exist in solution as well as in the solid state and interconvert reversibly by an intramolecular one-electron transfer between the metal ion and one quinone ligand in response to different external perturbations, such as temperature, pressure, and irradiation.[6−9] (See Scheme 1.)

Recently, we reported how this valence tautomeric complex may be converted into an array of four states that interconvert reversibly by using an additional reversible reduction process.[10] Such a strategy has been shown to be very useful for the systematic tuning of the critical temperature (T_c), at which there are equal amounts of both tautomers, as well as of the net magnetic moments and optical properties of the tautomeric isomers. In the previous study,[10] we were not able to establish a similar array of four states when an oxidation process was employed. In fact, oxidation of [Co^{II}(N-N)(DBSQ)$_2$] to [Co^{II}-(N-N)(DBSQ)(DBQ)]$^+$ resulted in the loss of the neutral quinone ligand to give [Co^{III}(N-N)$_2$(DBCat)][PF$_6$].[11]

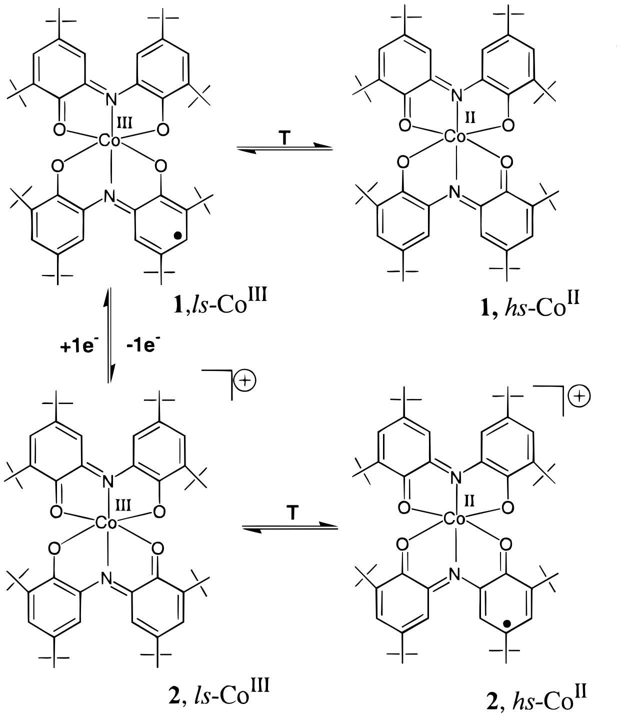
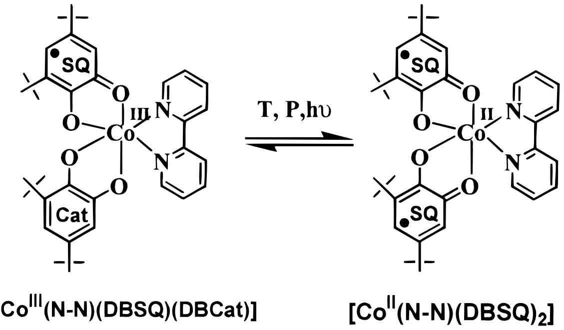


Figure 1. Diagram of the redox-tunable valence tautomerism of complex **2**. Complexes **1** and **2** each undergo a valence-tautomeric interconversion between two isomeric forms, which at the same time are connected by reversible one-electron oxidation processes.

Scheme 1



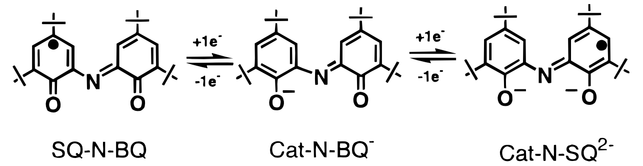
To overcome such problems, a new complex, namely [Co^{III}-(Cat-N-BQ)(Cat-N-SQ)] (**1**), where Cat-N-BQ$^-$ and Cat-N-SQ^{2-} refer respectively to the monoanionic and dianionic forms of the ((2-hydroxy-3,5-di-*tert*-butyl-1-phenyl)imino)-3,5-di-*tert*-butyl-1,2-benzoquinone ligand (Cat-N-BQ), can be used (see Figure 1). The advantage of complex **1**, which recently shown to exhibit valence tautomerism,[12] over the previously described [Co^{III}(N-N)(DBSQ)(DBCat)] complexes lies in the rich electrochemical behavior of the Schiff base ligand (see Scheme 2).

---

[1] (a) Institut de Ciència de Materials de Barcelona. (b) Universität Innsbruck. (c) University of California at San Diego.
[2] Kahn, O.; Launay, J. P. *Chemtronics* **1988**, *3*, 140.
[3] Hendrickson, D. N.; Adams, D. M.; Wu, C. C. In *Magnetism: A Supramolecular Function*; Kahn, O., Ed.; NATO ASI Series; Kluwer Publishing Co.; Dordrecht, The Netherlands, 1996; p 357.
[4] Gutlich, P.; Dei, A. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2734.
[5] Pierpont, C. G.; Lange, C. W. *Prog. Inorg. Chem.* **1994**, *41*, 331.
[6] Buchanan, R. M.; Pierpont, C. G. *J. Am. Chem. Soc.* **1980**, *102*, 4951.
[7] Roux, C.; Adams, D. M.; Itie, J. P.; Polina, A.; Hendrickson, D. N:, Verdaguer, M. *Inorg. Chem.* **1996**, *35*, 2846.
[8] Adams, D. M.; Li, B.; Simon, J. D.; Hendrickson, D. N. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1881.
[9] Adams, D. M.; Dei, A.; Rheingold, A. L.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1993**, *115*, 8221.
[10] Ruiz, D.; Yoo, J.; Guzei, I.; Rheingold, A.; Hendrickson D. N. *Chem. Commun.* **1998**, 2089.
[11] Ruiz, D.; Yoo, J.; Guzei, I.; Rheingold, A.; Hendrickson, D. N. unpublished results.
[12] Caneschi, A.; Cornia, A.; Dei, A. *Inorg. Chem.* **1998**, *37*, 3419.

10.1021/ic990714e CCC: $19.00

Scheme 2



This ligand can exist in different oxidation forms, ranging from +1 to −3, which may make it possible to obtain stable coordination complexes with different metal ions.[13]

In this note we report results of the first redox-tunable valence-tautomeric complex based on the reversible oxidation of complex **1**.

Results and Discussion

The cyclic voltammogram of complex **1** in CH_2Cl_2, with 0.1 M $NBu^n{}_4PF_6$ as supporting electrolyte, shows a one-electron oxidation process at $E_{1/2} = +0.18$ V (vs Ag/AgCl wire) and a reversible one-electron reduction at $E_{1/2} = -0.38$ V. Both $E_{1/2}$ values are comparable to previous values given in the literature and have been identified as being associated with electrochemical processes occurring at ligand-based orbitals.[13,14] Potential-controlled electrolysis experiments demonstrated the reversibility of both redox processes, indicating no structural changes such as ligand loss or decomposition on the time scale of the experiment. Therefore, the charged species formed from partial oxidation of complex **1** is capable of being generated chemically. Indeed, oxidation of **1**, prepared as previously described,[13] with 1 equiv of $AgBF_4$ yielded $[Co^{III}(Cat\text{-}N\text{-}BQ)_2][BF_4]$ (**2**,*ls*-Co^{III}). Magnetic measurements and X-ray studies of complex **2** in the solid state are fully consistent with the formulation $[Co^{III}(Cat\text{-}N\text{-}BQ)_2]^+$. Indeed, variable-temperature magnetic susceptibility data confirm the $S = 0$ magnetic ground state expected for a diamagnetic Co(III) complex with two Cat-N-BQ^- ligands with no unpaired electrons.

Single crystals suitable for X-ray diffraction analysis were obtained by slow diffusion of hexanes into a CH_2Cl_2 solution of complex **2**. A view of the molecular structure of complex (**2**,*ls*-Co^{III}) is given in Figure 2.

The results of the crystallographic study showed that the two ligands occupy meridional sites of an octahedron with average chelate bond distances that agree with the low-spin Co^{III} description. Indeed, the two equivalent ligands have Co−N and Co−O bond lengths of 1.851(3) and 1.918(2) Å, respectively. These values are in agreement with those previously found for $[Co^{III}(Cat\text{-}N\text{-}BQ)(Cat\text{-}N\text{-}SQ)]$ (**1**), with average Co−N and Co−O bond lengths of 1.868 and 1.896 Å, respectively,[13] and other $[Co^{III}(N\text{-}N)(DBSQ)(DBCat)]$ complexes with Co−O bond lengths that range from 1.851(6) to 1.906(6) Å.[9] Bond lengths to Co(II) have been shown to be typically 0.2 Å longer than bonds to oxygen donor ligands coordinated to Co(III).

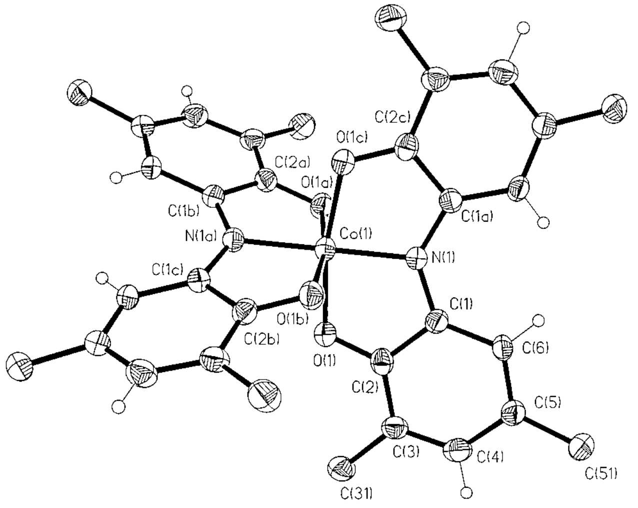


Figure 2. Illustration of the molecular structure of the cationic complex in $[Co^{III}(Cat\text{-}N\text{-}BQ)_2][BF_4]$ (**2**,*ls*-Co^{III}) at 218 K. The hydrogen atoms are omitted for clarity.

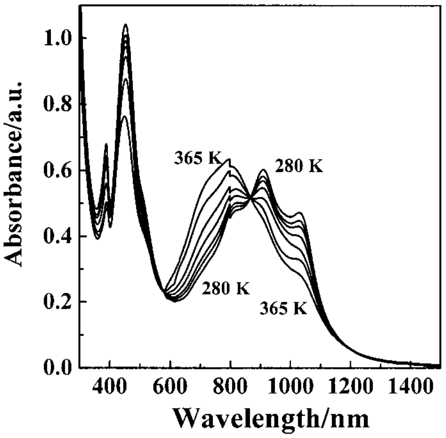


Figure 3. Temperature dependence of the electronic absorption spectrum of a toluene solution of complex **2**.

Finally, the variable-temperature absorption spectra of a toluene solution of complex **2**, depicted in Figure 3, show the existence of an equilibrium consistent with the valence tautomerism

$$\underset{\mathbf{2},ls\text{-}Co^{III}}{[Co^{III}(Cat\text{-}N\text{-}BQ)_2]^+} \rightleftharpoons \underset{\mathbf{2},hs\text{-}Co^{II}}{[Co^{II}(Cat\text{-}N\text{-}BQ)(SQ\text{-}N\text{-}BQ)]^+} \quad (1)$$

At low temperatures (280 K), where complex **2** is mostly in the (**2**,*ls*-$Co^{III})^+$ form, there is an intense band around 405 nm and a second set of three less intense transitions centered at 830, 910, and 1030 nm. Increasing the temperature converts $[Co^{III}(Cat\text{-}N\text{-}BQ)_2][BF_4]$ (**2**,*ls*-Co^{III}) to $[Co^{II}(Cat\text{-}N\text{-}BQ)(SQ\text{-}N\text{-}BQ)][BF_4]$ (**2**,*hs*-Co^{II}).

As a consequence, an increase in temperature from 280 to 365 K leads to a decrease of the intensity of the bands characteristic of the (**2**,*ls*-$Co^{III})^+$ isomer and a band at 790 nm, which is characteristic of the (**2**,*hs*-$Co^{II})^+$ isomer, appears. Two isosbestic points at 577 and 865 nm also appear, indicating that two species are interconverting in solution. The thermodynamic quantities ΔH and ΔS associated with equilibrium 1 were also determined by following the method described by Pierpont.[15] In such a method, the relative concentration of the two complexes present in solution at each temperature is obtained by monitoring changes in spectral data intensity. The thermodynamic quantities obtained were $\Delta H = +52.7$ kJ mol^{-1} and

---

[13] Larsen, S. K.; Pierpont, C. G. *J. Am. Chem. Soc.* **1988**, *110*, 1827.

[14] In a previous communication, Kadish reported the isolation of the first oxidation product derived from complex **1**: Maiya, B. G.; Deng, Y.; Kadish, K. M. *J. Chem. Soc., Dalton Trans.* **1990**, 3571. The authors postulated that the first one-electron oxidation of complex **1** would produce $[Co^{III}(Cat\text{-}N\text{-}BQ)_2]^+$, although electrochemical and ESR experiments were consistent in indicating that the one-electron oxidation generated $[Co^{III}(SQ\text{-}N\text{-}BQ)(Cat\text{-}N\text{-}SQ)]^+$. We believe the presence of a small proportion of the corresponding *hs*-Co^{II} tautomer could chiefly explain this fact.

[15] (a) Pierpont, C. G.; Jung, O. S. *Inorg. Chem.* **1995**, *34*, 1481. (b) Jung, O. S.; Pierpont, C. G. *Inorg. Chem.* **1994**, *33*, 2227.

Table 1. Crystal Data for $[\mathrm{Co^{III}(Cat\text{-}N\text{-}BQ)_2}][\mathrm{BF_4}]$ (**2**,*ls*-Co$^{\mathrm{III}}$)

empirical formula	$C_{56}H_{80}BCoF_4N_2O_4$
fw	990.96
crystal system	tetragonal
space group	$I\bar{4}c2$
a (Å)	19.577(6)
b (Å)	19.577(6),
c (Å)	15.466(7)
α (deg)	90
β (deg)	90
γ (deg)	90
V(nm^3)	5.928(4)
Z	4
D_{calc} (mg/m^3)	1.110
crystal size (mm^3)	0.85 × 0.29 × 0.26
temp (K)	218(2)
θ range, deg	2.63−23.49
R1	0.0451
wR2	0.1194

$\Delta S = +160.6$ J mol^{-1} K^{-1}, which were higher than those reported for valence tautomeric equilibrium of complex **1** ($\Delta H = +42.0$ kJ mol^{-1} and $\Delta S = +140.0$ J mol^{-1} K^{-1}). Since the interconversion between valence tautomers is an entropy-driven process,[16] the thermal population of tautomeric isomers is dictated by the Gibbs free energy difference, ΔG, where

$$\Delta G = \Delta G_{hs-\mathrm{Co^{II}}} - \Delta G_{ls-\mathrm{Co^{III}}} = \Delta H - T\Delta S \qquad (2)$$

Thus, at low temperatures, $T\Delta S$ is negligible compared to ΔH, and consequently only the *ls*-Co$^{\mathrm{III}}$ isomer is populated. However at high temperatures, ΔS is not negligible and the *hs*-Co$^{\mathrm{II}}$ tautomeric isomer becomes almost completely populated. The critical temperature (T_c), at which there are equal amounts of the (**2**,*ls*-Co$^{\mathrm{III}}$) and (**2**,*hs*-Co$^{\mathrm{II}}$) tautomeric forms, was found to be ∼328 K. This value is about 28 K higher than that reported for the corresponding complex **1**,[12] confirming that the ligand oxidation is a valuable tool for tuning valence tautomerism. The increase of the energy (i.e., enthalpy) separation between tautomeric forms will lead to an increase in the values of T_c. This explains the trend seen for **1** ($\Delta H = +42.0$ kJ mol^{-1}) and **2** ($\Delta H = +52.7$ kJ mol^{-1}), as well as those previously reported for other Co(N-N)(diox)$_2$ complexes.[17]

No interconversion in the solid state was observed, as evidenced by the lack of changes in the variable magnetic susceptibility data. Probably, the main reason is the absence of solvate molecules in complex **2**, as confirmed by its X-ray structure, which have been found to play a critical role in determining the transformation in the solid state.[9]

In conclusion, the synthesis, characterization, and study of complex **2** as a stable species allowed us to establish a new switching molecular array, depicted in Figure 1, that interconverts reversibly either by thermal means (valence tautomerism) or by a reversible oxidation process.

Table 2. Selected Average Bond Lengths (Å) and Angles (deg) for $[\mathrm{Co^{III}(Cat\text{-}N\text{-}BQ)_2}][\mathrm{BF_4}]$ (**2**,*ls*-Co$^{\mathrm{III}}$)

Bond Lengths			
Co(1)−N(1a)	1.851(3)	Co(1)−N(1)	1.851(3)
Co(1)−O(1b)	1.918(2)	Co(1)−O(1a)	1.918(2)
Co(1)−O(1)	1.918(2)	Co(1)−O(1c)	1.918(2)
O(1)−C(2)	1.304(4)	N(1)−C(1a)	1.353(4)
N(1)−C(1)	1.353(4)	C(1)−C(6)	1.425(5)
C(1)−C(2)	1.453(5)	C(2)−C(3)	1.436(5)
C(3)−C(4)	1.371(5)	C(3)−C(31)	1.539(5)
C(4)−C(5)	1.448(5)	C(5)−C(6)	1.360(5)
Bond Angles			
N(1a)−Co(1)−N(1)	180.0	O(1b)−Co(1)−O(1a)	169.44(14)
N(1a)−Co(1)−O(1b)	84.72(7)	N(1a)−Co(1)−O(1)	95.28(7)
N(1)−Co(1)−O(1b)	95.28(7)	N(1)−Co(1)−O(1)	84.72(7)
N(1a)−Co(1)−O(1a)	84.72(7)	O(1b)−Co(1)−O(1)	86.93(14)
N(1)−Co(1)−O(1a)	95.28(7)	O(1a)−Co(1)−O(1)	94.05(13)

Experimental Section

Reagents were purchased from commercial laboratory supply houses. Solvents were distilled prior to use. All manipulations were performed in contact with the atmosphere. The starting complex **1** was prepared according to the literature method.[13]

Physical Measurements. Electronic absorption spectra were recorded with a Varian Cary 05E spectrophotometer, provided with a multicell block and equipped with an ER 4121HT temperature controller. Spectra were collected after the sample had been allowed to thermally equilibrate at each temperature for more than 10 min. Direct current magnetic susceptibility measurements were carried out on a Quantum Design MPMS SQUID susceptometer having a 55 kG magnet and operating in the range 4−300 K. Electrochemical experiments were carried out on an EG&G Princeton Applied Research model 263A potentiostat/galvanostat, using an Ag/Ag$^+$ electrode as the reference electrode and a platinum wire as the counter electrode. Tetrabutylammonium hexafluorophosphate was used as the supporting electrolyte.

X-ray Measurements. X-ray data were collected at 218 K on a Bruker P4 diffractometer with monochromatic Mo Kα ($\lambda = 0.710\,73$ Å) radiation. Data were collected via ω scans and corrected for Lorentz and polarization effects but not for absorption. The structures were all refined by a full-matrix least-squares methods. Crystal data and selected average bond distances and angles are given in Tables 1 and 2. Atomic coordinates and other related structural data have been deposited as Supporting Information.

$[\mathrm{Co^{III}(Cat\text{-}N\text{-}BQ)_2}][\mathrm{BF_4}]$ (2,*ls*-Co$^{\mathrm{III}}$). A sample of $[\mathrm{Co^{III}(Cat\text{-}N\text{-}BQ)(Cat\text{-}N\text{-}SQ)}]$ (**1**) (300 mg; 3.03×10^{-4} mol), synthesized as previously described, was dissolved in CH_2Cl_2 at room temperature. To this solution was added $AgBF_4$ (59 mg; 3.03×10^{-4} mol). The mixture was stirred for 2 h. After removal of the Ag metal, a dark yellow-brown crystalline material was obtained after evaporation of the solution. Single crystals suitable for X-ray analysis were obtained by slow diffusion of hexane into a CH_2Cl_2 solution of complex **2** (40% yield). Anal. Calcd for $C_{56}H_{80}BCoF_4N_2O_4$: C, 67.9; H, 8.1; N, 2.8. Found: C, 68.3; H, 8.3; N, 2.4.

Acknowledgment. This work was supported by the DGES (Grant PB96-0862-C02-01), the CIRIT (Grant 1998SGR-00106), the National Science Foundation, and the 3MD Network of the TMR Program of the EU (Contract ERBFMRXCT 980181). D.R-M. is grateful to the Generalitat de Catalunya for a postdoctoral grant.

Supporting Information Available: Tables of X-ray experimental details, atomic coordinates, thermal parameters, and bond distances and angles for complex **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

IC990714E

---

(16) The valence tautomerism is characterized by a large entropy gain that arises owing to the following: (1) The valence tautomeric interconversion from *ls*-Co$^{\mathrm{III}}$ to *hs*-Co$^{\mathrm{II}}$ leads to a gain in electronic entropy due to the higher spin state degeneracy of the *hs*-Co$^{\mathrm{II}}$ form. (2) The longer metal−ligand bond lengths of the *hs*-Co$^{\mathrm{II}}$ tautomer result in lower energy vibrations and a higher density of vibrational states in the *hs*-Co$^{\mathrm{II}}$ form than in the *ls*-Co$^{\mathrm{III}}$ form.

(17) Adams, D. M.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1996**, *118*, 11515.