Valence tautomeric cobalt *o*-quinone complexes in a dual-mode switching array

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The characterization of valence tautomeric cobalt complexes with an array of four states, each with different optical and magnetic properties, is reported and it is shown that they can interconvert reversibly between the four states either thermally or by redox processes.

Complexes of the composition [Co(3,5-DTBCat)(3,5-DTBSQ)(NN)], where 3,5-DTBCat^{2-} and 3,5-DTBSQ^{-} refer, respectively, to the catecholate (Cat^{2-}) and semiquinonate (SQ^{-}) forms of 3,5-di-*tert*-butyl-*o*-quinone, and NN is a chelating diiminium ligand such as 2,2′-bipyridine (bpy, complex **1**) or 1,10-phenanthroline (phen, complex **2**), exhibit valence tautomerism.[1,2] These complexes can be interconverted in solution or in the solid state by means of different external stimuli such as temperature, pressure or irradiation between a high-spin [Co^{II}(SQ)$_2$(NN)] (*hs*-Co^{II}) or a low-spin [Co^{III}(Cat)(SQ)(NN)] (*ls*-Co^{III}) form with appreciable changes in their electronic absorption spectra and magnetic ground states.[3–6] In solution, the equilibrium in eqn. (1) can be induced by variations of temperature and monitored by UV–VIS spectroscopy.

$$[\mathrm{Co^{III}(SQ)(Cat)(NN)}]\ (ls\text{-}\mathrm{Co^{III}}) \rightleftharpoons [\mathrm{Co^{II}(SQ)_2(NN)}]\ (hs\text{-}\mathrm{Co^{II}}) \qquad (1)$$

At low temperatures, there is a band at ≈ 600 nm characteristic of the *ls*-Co^{III} tautomer. As the temperature of the solution is increased the intensity of the 600 nm band decreases and a band at ≈ 770 nm characteristic of the *hs*-Co^{II} tautomer increases in intensity. Here we report how this valence tautomerism equilibrium may be converted into an array of four states with different magnetic and optical properties that interconvert reversibly between them, where the additional switching capacity results from an electrochemical process.

The reversible redox characteristics of complexes **1** and **2** were employed to develop the square array shown in Fig. 1. A CH$_2$Cl$_2$ solution of complex **1** at 273 K with 0.1 M NBu$^n_4$PF$_6$ as a supporting electrolyte is mostly in the **1**,*ls*-Co^{III} form, as determined by UV–VIS spectroscopy. The CV of **1**,*ls*-Co^{III} under these conditions exhibits a reversible reduction at $E_0 = -0.34$ and a reversible oxidation at +0.25 V *vs*. a Ag wire (E_0 of ferrocene under the same experimental conditions is +0.36 V). Previous studies of different *o*-quinone metal complexes have shown that the redox processes occur at the quinone ligands.[7] Therefore, the first process at −0.34 V for complex **1**,*ls*-Co^{III} involves the reduction of the semiquinonate ligand to the catecholate form, whereas the second process involves the oxidation of the catecholate ligand of **1**,*ls*-Co^{III} to the semiquinonate ligand form. A CH$_2$Cl$_2$ solution of complex **2** at 305 K with 0.1 M NBu$^n_4$PF$_6$ as a supporting electrolyte is mostly in the **2**,*hs*-Co^{II} form. The CV of **2**,*hs*-Co^{II} exhibits a reduction process at $E_0 = -0.2$ V *vs*. a Ag wire. This process corresponds to the reduction of both semiquinonate ligands to catecholate ligands. Examination of the scan rate (υ) dependences for the processes observed for both tautomers showed a linear dependence of the peak current with respect to $\upsilon^{1/2}$, indicating that these redox processes are diffusive. Constant-potential electrolysis experiments have confirmed the reversibility of the different processes. Thus, both of the valence tautomers in eqn. (1) can be reduced reversibly. This allowed us to establish the square array shown in Fig. 1.

Treatment of complex **1**,*ls*-Co^{III} in CH$_2$Cl$_2$ at 273 K with 1 equivalent of Co(Cp)$_2$ yielded [Co(Cp)$_2$][Co^{III}(3,5-DTBCat)$_2$(bpy)] (**3**,*ls*-Co^{III}) as a dark-green polycrystalline solid (70% yield).† The $S = 0$ ground state was confirmed by variable-field magnetization data collected at 2.3 and 5.0 K. The presence of two catecholate ligands was also confirmed by an increase (relative to complex **1**) in the intensity of the characteristic catecholate C–O IR bands seen at ≈ 1250 cm^{-1}. Our interest in complex **3** was considerably enhanced when it was found that the electronic absorption spectrum of this complex in acetone exhibited a temperature dependence consistent with the following valence-tautomeric equilibrium:

$$[\mathrm{Co^{III}(Cat)_2(bpy)}]^-\ (\mathbf{3},ls\text{-}\mathrm{Co^{III}}) \rightleftharpoons [\mathrm{Co^{II}(SQ)(Cat)(bpy)}]^-\ (\mathbf{3},hs\text{-}\mathrm{Co^{II}}) \qquad (2)$$

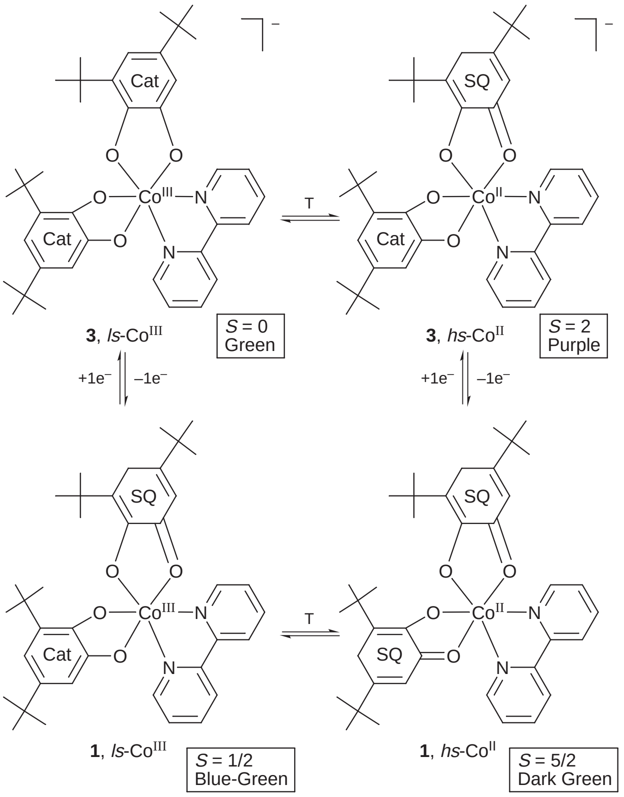

Fig. 1 Diagram of a dual-mode switching array. Complexes **1** and **3** each undergo a valence tautomeric interconversion and the tautomers of complex **3** are obtained reversibly by one-electron reduction of the tautomers of complex **1**. An array of four different states with different optical and magnetic ground states is then obtained.

As shown in Fig. 2, at low temperatures there is an intense band at 405 nm and a second less intense transition at 610 nm, where both bands are characteristic of the (**3**,*ls*-Co^{III})$^-$ isomer. Increasing the temperature converts this *ls*-Co^{III} tautomer to the [Co^{II}(3,5-DTBSQ)(3,5-DTBCat)(bpy)]$^-$ tautomer, identified as (**3**,*hs*-Co^{II})$^-$. The acetone solution changes from green at low temperatures to purple at higher temperatures. Two isosbestic points are seen at 360 and 470 nm, indicating that there are two species in equilibrium. When the sample was cooled, the spectrum characteristic of the (**3**,*ls*-Co^{III})$^-$ form was recovered. The cycle was repeated several times, confirming the reversibility of the interconversion although a gradual decrease of the absorbance was observed due to decomposition of the *hs*-Co^{II} form that reacts even with traces of oxygen. A toluene solution of complex **1** at high temperatures is mostly in the **1**,*hs*-Co^{II} form as confirmed by UV–VIS spectroscopy. Therefore, direct reaction of a toluene solution of complex **1** with 1 equivalent of Co(Cp)$_2$ was used to directly give [Co(Cp)$_2$][Co^{II}(3,5-DTBSQ)(3,5-DTBCat)(bpy)] (**3**,*hs*-Co^{II}) as a purple precipitate obtained after filtration from the solution (20% yield).† This solid is highly air-sensitive, however, it was characterized by variable-temperature magnetic susceptibility, electronic absorption and EPR spectroscopies. The value of μ_{eff} varies gradually from 4.24 μ_B at 320 K to 4.04 μ_B at 70.0 K, whereupon there is an increase to 5.14 μ_B at 20.0 K, followed by a decrease to 3.07 μ_B at 3.0 K. These results are consistent with a *hs*-Co^{II}(S = 3/2) complex with one S = 1/2 semiquinonate ligand, where there is a weak ferromagnetic exchange interaction between the ligand and the metal. Dissolution of **3**,*hs*-Co^{II} in acetone gave the same reversible temperature dependence in the UV–VIS electronic spectrum as shown in Fig. 2 for (**3**,*ls*-Co^{III})$^-$, confirming the existence of the valence tautomeric equilibrium **3**,*ls*-Co^{III-} $\rightleftharpoons$ **3**,*hs*-Co^{II-}. X-Band EPR spectra showed the eight-line cobalt hyperfine splitting characteristic of Co–quinone systems [A(Co) $\approx$ 12 G]. Finally, it must be emphasized that additional constant-potential electrolysis experiments confirmed the reoxidation of the anionic complexes to the neutral species demonstrating the validity of the array detailed in Fig. 1. Thus, an array of four states is controlled by two temperature-controlled valence tautomeric equilibria and two reversible redox processes. The possibility of entering the cycle at each state and advancing through the square array in a clockwise and counter-clockwise direction was also established.

Reduction of complex **2** with 1 equivalent of Co(Cp)$_2$ in CH$_2$Cl$_2$ and toluene gave the tautomers [Co(Cp)$_2$][Co^{III}(3,5-DTBCat)$_2$(phen)] (**4**,*ls*-Co^{III}) and [Co(Cp)$_2$][Co^{II}(3,5-DTBSQ)(3,5-DTBCat)(phen)] (**4**,*hs*-Co^{II}).† The magnetic and spectroscopic characterization as well as the variable-temperature UV–VIS spectra of acetone solutions of these two phen Co(Cp)$_2^+$ salts were also found to be similar to those obtained for the corresponding bpy complexes. In short, the neutral phen complex **2** can be reduced and the reduced Co^{III} and Co^{II} species are involved in a valence-tautomeric equilibrium, *i.e.* **4**,*ls*-Co^{III-} $\rightleftharpoons$ **4**,*hs*-Co^{II-}, establishing a similar array of four states for the phen complex.

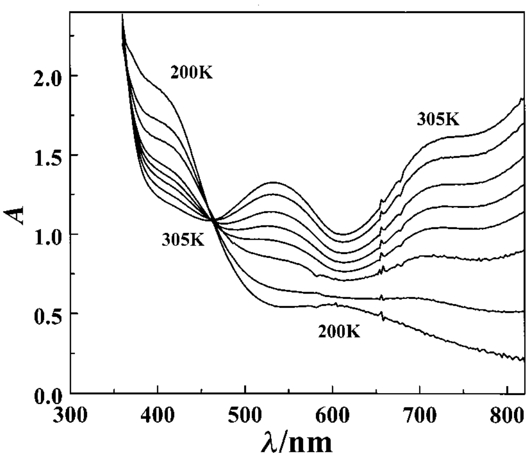

Fig. 2 Temperature dependence of the electronic absorption spectrum of an acetone solution of complex **3**

Oxidation of complex **1** could also establish another valence-tautomeric equilibrium, in addition to the two pictured in Fig. 1. Toward this goal, complex **1** was oxidized in 95% ethanol at 273 K (where complex **1** is mostly in the **1**,*ls*-Co^{III} form) by a H$_2$O$_2$–HCl mixture, following a procedure described by Wicklund *et al.*[8] for the oxidation of catecholate ligands. This oxidation gave [Co^{III}(3,5-DTBSQ)$_2$(bpy)]Cl, the Cl$^-$ salt of (**5**,*ls*-Co^{III})$^+$.† Variable-temperature UV–VIS spectroscopy provides convincing evidence of the presence of a valence-tautomeric equilibrium for the oxidized form of the bpy complex in EtOH, *i.e.* for the equilibrium of **5**,*ls*-Co^{III+} $\rightleftharpoons$ **5**,*hs*-Co^{II+}. At low temperatures (200 K) an intense band at 570 nm is seen that is characteristic of the (**5**,*ls*-Co^{III})$^+$ tautomer. An increase in temperature to 300 K leads to a decrease in the intensity of this band as a band at 720 nm, that is characteristic of (**5**,*hs*-Co^{II})$^+$, grows in. Two isosbestic points are seen. However, we must emphasize that when the temperature of the EtOH solution of (**5**,*hs*-Co^{II})$^+$ is increased above 300 K, the intensity of the 720 nm band does not increase. Instead, the intensities of both the 720 and 570 nm bands decreased as the temperature was increased above 300 K. We attribute this thermal instability of (**5**,*hs*-Co^{II})$^+$ to loss of the quinone ligand.

In summary, complexes of the composition [Co(Cp$_2$)]-[Co^{III}(3,5-DTBCat)$_2$(NN)] have been shown to undergo valence tautomerism. In addition, the reversibility of the tautomeric equilibria permitted the establishment of an array of four states with different magnetic and optical properties, reversibly interconvertible by means of electrochemical and thermal switching. Such an array of states is suitable to be used in the future as a building block for molecular electronic devices.

Notes and References

† The complex [Co(Cp)$_2$][Co^{III}(3,5-DTBCat)$_2$(bpy)] (**3**,*ls*-Co^{III}) analyzed satisfactorily (C,H,N). [Found: C, 68.07; H, 7.04; N, 3.63. C$_{48}$H$_{58}$N$_2$O$_4$Co$_2$ requires C, 68.23; H, 6.93; N, 3.31%]. The complex [Co(Cp)$_2$][Co^{II}(3,5-DTBSQ)(3,5-DTBCat)(bpy)] (**3**,*hs*-Co^{II}) analyzed satisfactorily (C,H,N). [Found: C, 56.86; H, 6.91; N, 3.12. C$_{48}$H$_{58}$N$_2$O$_4$Co$_2$ requires C, 68.23; H, 6.93; N, 3.31%]. The complex [Co(Cp)$_2$][Co^{III}(3,5-DTBCat)$_2$(phen)] (**4**,*ls*-Co^{III}) analyzed satisfactorily (C,H,N). [Found: C, 69.90; H, 6.55; N, 2.88. C$_{50}$H$_{58}$N$_2$O$_4$Co$_2$ requires C, 69.10; H, 6.70; N, 3.20%]. The complex [Co^{III}(3,5-DTBSQ)$_2$(bpy)]Cl (**5**,*ls*-Co^{III}) analyzed satisfactorily (C,H,N). [Found: C, 65.35; H, 7.18; N, 4.28. C$_{38}$H$_{48}$N$_2$O$_4$CoCl requires C, 65.80; H, 7.00; N, 4.04%]. The complex [Co(3,5-DTBCat)(bpy)$_2$](BF$_4$)·2CH$_2$Cl$_2$ (**6**) analyzed satisfactorily (C, H, N). [Found: C, 59.00; H, 5.60; N, 7.90. C$_{34}$H$_{40}$N$_4$O$_2$CoBF$_4$ requires C, 59.80; H, 5.80; N, 8.20%].

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