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Dinuclear Cobalt Bis(dioxolene) Complex Exhibiting Two Sequential Thermally Induced Valence Tautomeric Transitions

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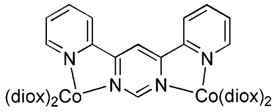
4,6-Di-2′-pyridylpyrimidine is employed as a bis(diimine) ligand bridging two cobalt bis(dioxolene) centers. The thermally induced valence tautomeric transitions of these two metal centers are coupled through the ligand. The result is that sequential switching from high-spin Co^{II} to low-spin Co^{III} of one center, followed by the onset of switching of the other center at lower temperature, is observed in a solid amorphous thin film by IR absorption spectroscopy.

One of the foremost goals in the pursuit of new molecular materials is the design of compounds that exhibit electronic bistability, the property existing in one of two electronic states depending on externally applied conditions.[1] It is commonly acknowledged that such materials have potential applications for future electronic devices. The phenomenon of valence tautomerism (VT), an intramolecular electron transfer often accompanied by spin crossover, is a well-known example of electronic bistability, often induced by variation in the applied temperature.[2]

VT has been observed in a wide variety of cobalt bis(dioxolene) diimine complexes.[3] The low-temperature state is low-spin Co^{III}(SQ)(Cat)(NN), where SQ is a dioxolene ligand in a semiquinonato oxidation state, Cat is a dioxolene ligand in a catecholato oxidation state, and NN is a diimine ligand such as 2,2′-bipyrimidine. The VT transition involves an intramolecular electron transfer that results in the oxidation of the Cat ligand to an SQ ligand and the reduction of Co^{III} to Co^{II}, accompanied by spin crossover such that the high-temperature state is high-spin $Co^{II}(SQ)_2(NN)$.

Recently, several dinuclear cobalt (bis)dioxolene valence tautomers have been reported. Designs include the use of 2,2′-bipyrimidine as the diimine ligand,[4] the synthesis of a dinuclear cobalt tetraoxolene complex,[5] dinuclear cobalt complexes of extended conjugated bis(dioxolene) ligands,[6] and most recently dinuclear cobalt complexes of extended diimine ligands.[7] Although, in principle, these dinuclear valence tautomers constitute potential designs for a tristable molecular switch, none of these complexes are reported to exhibit all three possible states, $(Co^{II})_2$, $[(Co^{II})(Co^{III})]$, and $(Co^{III})_2$, over a given temperature range observed using a single experimental technique. Herein we provide the first observation, using near-IR absorption spectroscopy, of switching in the solid state between the $(Co^{II})_2$ and $[(Co^{II})(Co^{III})]$ states, followed by the onset of switching to the $(Co^{III})_2$ state in a dinuclear cobalt bis(dioxolene) complex **1** using 4,6-di-2′-pyridylpyrimidine as the diimine ligand.



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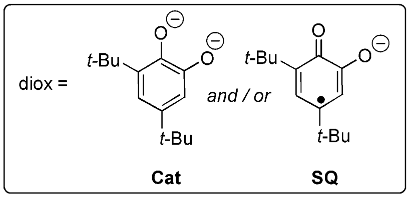

Complex **1** was prepared by adding a solution of $Co_2(CO)_8$ in dry cyclohexane to a solution of 3,5-di-*tert*-butyl-1,2-

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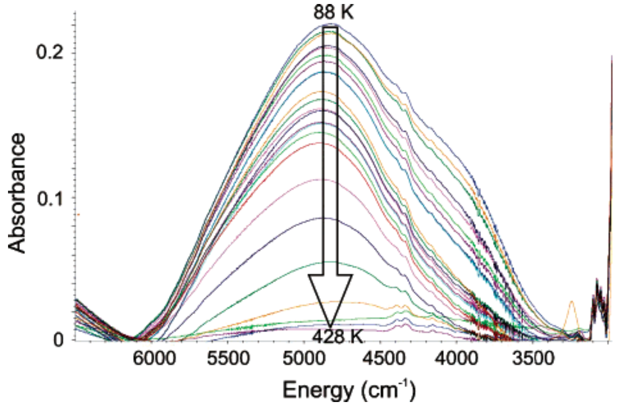

Figure 1. Absorption measurements of the IVCT band of a thin film of **1** on a CaF_2 plate at various temperatures from 88 to 428 K.

benzoquinone and 4,6-di-2′-pyridylpyrimidine in dry cyclohexane under an Ar(g) atmosphere, yielding **1** as a black precipitate (35.1%).

The intervalence charge-transfer (IVCT) band of an amorphous film (no peaks in X-ray powder diffraction, XRPD) of **1** was observed as a function of temperature from 88 to 428 K. The film was prepared by evaporation of a CH_2Cl_2 solution onto a single-crystal CaF_2 plate under Ar(g) and submitted to a dynamic vacuum (10^{-2} Torr) in the instrument cavity for 15 min prior to and throughout the duration of the measurements. Multiple films were tested with multiple temperature cycles in order to ensure reproducibility. Representative data are shown. The IVCT band occurs in the near-IR region (centered at 4900 cm^{-1}) of the absorption spectrum (Figure 1) and arises from ligand mixed valency in the Co^{III}(SQ)(Cat) unit.[8] Because IVCT is not expected for a $Co^{II}(SQ)_2$ unit, the intensity of the IVCT absorption band can be directly correlated to the concentration of Co^{III} in the sample. We also observe a broad shoulder in our lower temperature spectra, centered at 3900 cm^{-1}, that has not been observed in previously reported cobalt bis(dioxolene) valence tautomers. The asymmetric shape of the higher temperature spectra suggests that there may be another low-intensity absorption centered at 5500 cm^{-1}. To deconvolute these three absorptions, the spectra were modeled using four fitting equations: three mixed Gaussian−Lorentzian functions and a linear baseline equation (Figure 2), as provided in the Grams/AI(7.02) modeling software package.

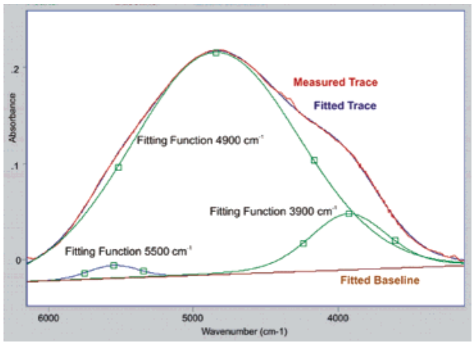

Figure 2. Measured absorption at 108 K and the fitted trace derived from Gaussian−Lorentzian functions at 5500, 4900, and 3900 cm^{-1} and a linear baseline function.

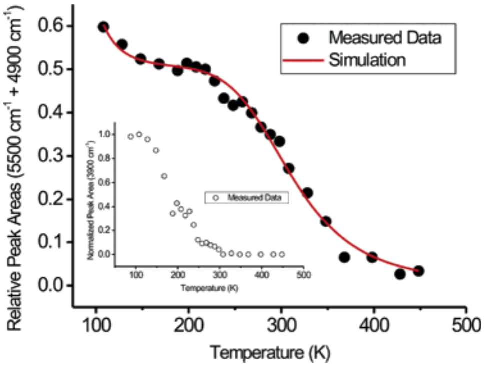

Figure 3. Temperature dependence of the IVCT band at 4900 cm^{-1} plotted as the normalized area under the absorption curve (●) and simulated fit (—). The inset is the IVCT band at 3900 cm^{-1} plotted as the normalized area under the absorption curve as a function of temperature (○).

At high temperatures (upward of ca. 400 K), the near-IR absorption intensity approaches zero, indicating that Co sites are predominantly in a 2+ oxidation state [i.e., $(Co^{II})_2$ state]. At lower temperatures, the IVCT band is observed, indicating the presence of the Co^{III} sites. Plotting the peak areas of all three modeled peaks as a function of temperature reveals that the absorptions at 4900 and 3900 cm^{-1} are temperature-dependent but the absorption at 5500 cm^{-1} is not. The absorption at 5500 cm^{-1} may be an undetected minor impurity, or it may be a mathematical requirement of the peak-fitting process because the real absorptions may not be strictly Gaussian−Lorentzian in shape. Because it does not vary with temperature and therefore should have no effect on the relative absorption intensities as a function of temperature, we have opted to include the area of the 5500-cm^{-1} peak into the area of the 4900-cm^{-1} peak in order to decrease the error inherent in fitting a low-intensity peak buried under a larger peak. The plot of the relative intensity as a function of temperature for the 4900-cm^{-1} peak reveals a sigmoidal shape with a plateaulike feature at lower temperatures (ca. 125−225 K) and a clear upward trend below 125 K. This plateau can be assigned to the partial isolation of the $[(Co^{II})(Co^{III})]$ state because a further decrease in the temperature results in a further increase in the absorption intensity, indicating the onset of switching to the $(Co^{III})_2$ state. As such, we have plotted the relative absorptions of the 4900-cm^{-1} peak, assuming that the approximate midpoint of the plateaulike feature (ca. 175 K) represents half of the Co sites in the 2+ oxidation state and half in the 3+ oxidation state (Figure 3.)

Plotting the relative absorption intensity of the 3900-cm^{-1} peak as a function of temperature also generates a sigmoidal curve. Interestingly, the relative intensity of this curve changes dramatically in the 125−225 K temperature range, the same range in which the 4900-cm^{-1} peak intensity plateaus. We suggest that the origin of this slightly lower energy peak may be IVCT between the SQ and Cat ligands of neighboring Co sites, which are likely in closer spatial proximity than the SQ and Cat ligands of a single Co^{III}(SQ)(Cat) unit. It should, then, be directly correlated to the amount

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Table 1. Thermodynamic Parameters Used To Fit IVCT Band Intensity Data for Complex **1**

	$\Delta H°$ (kcal mol^{-1})	$\Delta S°$ (cal K^{-1} mol^{-1})
K_1	1.3 ± 0.4	15.5 ± 3.9
K_2	5.3 ± 0.3	17.1 ± 1.2

of [(Co^{II})(Co^{III})] present in the sample and should not increase in intensity any further with the onset of switching to the (Co^{III})$_2$ state, as is observed.

The normalized absorption intensity of the 4900-cm^{-1} peak was fit using eq 1,

$$x_{\mathrm{Co^{III}}} = \frac{\dfrac{1}{K_1K_2} + \dfrac{1}{2K_2}}{\dfrac{1}{K_1K_2} + \dfrac{1}{K_2} + 1} \qquad (1)$$

where $x_{\mathrm{Co^{III}}}$ is the fraction of Co^{III} per metal site and K_1 and K_2 are the equilibrium constants that govern the three possible states:

$$(\mathrm{Co^{III}})_2 \underset{}{\overset{K_1}{\rightleftharpoons}} [(\mathrm{Co^{II}})(\mathrm{Co^{III}})] \overset{K_2}{\rightleftharpoons} (\mathrm{CO^{II}})_2$$

Thermodynamic parameters $\Delta H°$ and $\Delta S°$ for the two equilibria were set as variables in the fitting process using the equality $K_{\mathrm{eq}} = \exp(-\Delta H°/RT + \Delta S°/R)$. The optimized values are given in Table 1. The fit values for these thermodynamic parameters are small but still reasonable compared to those of previously reported cobalt bis(dioxolene) valence tautomers.[2,9]

In addition to the near-IR absorption measurements, the absorption spectra of a thin film of **1** on a CaF$_2$ plate were measured in the mid-IR (400−4000-cm^{-1}) region as a function of temperature. The expected spectral changes were observed. These include an absorption at 1285 cm^{-1} [lit.[6] ν(C−O) Cat] with significant intensity at lower temperatures and zero intensity at higher temperatures (see the Supporting Information). Attempts at measuring the absorption spectrum of a film as a function of temperature in the visible region (400−800 nm) generated inconclusive results. Although it appeared that the spectral features changed with temperature, the absorptions were very weak, probably owing to the “low concentration” of the thin film.

In addition to our investigations of the thin film, complex **1** was characterized in the solid state as an amorphous powder and as a toluene solution. The magnetic susceptibility of a solvent-free solid amorphous sample (no peaks in pressed-powder XRPD on an Al substrate) of **1** was measured by DC-SQUID at an applied field of 100 Oe over a 2−300 K temperature range (see the Supporting Information). In contrast to the thin-film IVCT measurements, only the [(Co^{II})(Co^{III})] state is observed by this method, with evidence of the onset of the (Co^{II})$_2$ state at higher temperatures, underscoring the importance of previous reports on the influence of the physical phase on the VT properties.[7] The amorphous powder was also characterized by X-band electron paramagnetic resonance (EPR) as a function of temperature. A broad peak, centered at $g = 2.006$, was observed over the entire measured temperature range without a significant decrease in the intensity (280−360 K), suggesting that, in constrast to the thin film, Co^{III} persists and the (Co^{II})$_2$ state is not realized in the powder sample at 360 K. This is in agreement with the magnetometry measurements.

Absorption measurements of a toluene solution of **1** were performed in the visible and near-IR regions as a function of temperature. A broad peak at 4900 cm^{-1} was observed to vary in intensity with temperature such that it diminished to near-zero intensity at 345 K and grew in intensity down to 194 K reproducibly over multiple temperature cycles. The signal-to-noise ratios for these spectra were much smaller than those of the thin film in the near-IR region, and modeling of distinct peaks was not reliable. Plots of the entire peak area as a function of temperature did not reveal any plateaulike features, nor did the peak intensity seem to be approaching a steady value at low temperature. These results suggest that, at high temperatures in a toluene solution, **1** achieves the (Co^{II})$_2$ state and that the onset of switching to the [(Co^{II})(Co^{III})] state is observed upon cooling. This is supported by the absorption spectra in the visible region, by ^{1}H NMR, and by EPR measurements in toluene as a function of temperature (see Supporting Information). Again the importance of the physical phase must be acknowledged.

Finally, preliminary cyclic voltammetry (CV) measurements in CH$_2$Cl$_2$ at room temperature (see the Supporting Information) reveal a rich redox manifold more complex than that previously reported for mononuclear species.[10] In particular, it appears that peaks assigned to the oxidation of the Cat ligand and reduction of the SQ ligand in the Co^{III} form of mononuclear species are split in the CV of **1**, as would be expected given electronic coupling between the two Co centers.

Results herein suggest the first observation of tristability in a dinuclear valence tautomer but only as a thin amorphous film. Two of the possible states, and the onset of the third, are observed by near-IR absorption spectroscopy through measurement of the IVCT band intensity in this physical phase.

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Supporting Information Available: Synthetic, spectroscopic, and magnetometric details and spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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