Complete Direct and Reverse Optically Induced Valence Tautomeric Interconversion in a Cobalt–Dioxolene Complex

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The investigation of systems undergoing intramolecular electron transfer (ET) processes involves two intriguing goals.[1–5] The first goal is the elucidation of factors controlling the efficiency of the process. The second concerns their potential technological application as molecular-scale devices. With this aim particular attention is devoted to molecules which may show interplay between charge mobility, magnetic properties and optical irradiation. The basic research work in the field has been developed with the synthesis of molecular systems containing two appropriate redox active units, provided that their electronic coupling is relatively small.

Typical examples of these systems are molecular mixed-valence complexes of class II containing two distinct sites.[6–9] In these molecules an external perturbation, like changes in temperature or optical irradiation, may induce an ET process affording a redox isomer of the initial compound. An appealing situation is encountered when the redox moieties are different, a situation found in cobalt–dioxolene complexes undergoing valence tautomerism (VT).[4,5,10–14] In the simplest case, that is, a 1:1 complex, this may exist in two well defined charge distributions with different magnetic properties: diamagnetic *ls*-cobalt(III)–catecholato and paramagnetic *hs*-cobalt(II)–semiquinonato.[15–19]

In recent publications we have shown how the charge distribution of a series of cobalt–dioxolene complexes of formula [Co(Me$_n$tpa)(diox)](PF$_6$) (Me$_n$tpa = methyl derivatives of tris(2-pyridylmethyl)amine, diox = catecholato (Cat) or semiquinonato (SQ) forms of *o*-quinones) can be qualita-

tively related to the difference between the redox potentials of the metal acceptor and of the coordinated dioxolene ligand, which can be independently observed in a series of appropriate reference compounds.[17,18] This allowed us to justify the observation of entropy driven valence tautomeric interconversion for some of these complexes as well as the trend of the relaxation decay rates of the optically induced metastable redox isomers at cryogenic temperatures. The observed data showed that the intramolecular ET process in these 1:1 adducts were, as expected, extremely sensitive to lattice energies. This observation was not surprising since it was expected that free energy of the ET process should be strongly dependent on vibronic coupling with the environment.[20–23] For this reason we decided to synthesize different solvates of the [Co(Me$_2$tpa)(DBCat)](PF$_6$) complex (**1**, DBCat = 3,5-di-*tert*-butylcatecolato) which was observed to undergo both entropy driven and optically induced valence tautomerism. The results we obtained for the toluene solvate provide, when compared to those previously reported for other derivatives,[17,18] an intriguing benchmark for the description of these systems.

The temperature dependence of the magnetic susceptibility of **1** is shown in Figure 1. At low temperatures the $\chi_M T$ value (0.25 emu K mol^{-1}) is consistent with a Co^{III}–Cat charge distribution, the residual paramagnetism being attributable to the TIP of Co^{III} and to an unavoidable presence of high-spin fraction. Around 100 K the $\chi_M T$ value starts to rise, which indicates the occurrence of a thermally induced valence tautomeric process; this results, above 270 K, in Co^{II}–SQ charge distribution. The value observed ($\chi_M T = 2.96$ emu K mol^{-1}) at 300 K is indeed in agreement with what is expected for the sum of the two contribution of uncoupled Co^{II} ($2.6 < \chi_M T < 3.1$ emu K mol^{-1}) and a radical species ($\chi_M T = 0.375$ emu K mol^{-1}) as well as with previous reports.[24] An intriguing and hitherto unreported feature for valence tautomeric interconversion processes is clearly evidenced in the transition region: the transformation between the two redox isomers takes place in two separated steps at 125 and 185 K (inset of Figure 1) with a plateau centered at 155 K, where 50% of conversion occurs. The two-step char-

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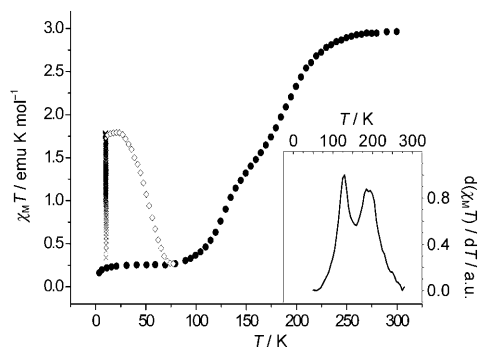Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.200801120.

Figure 1. $\chi_M T$ vs T for **1** measured before (●) and after (◇) irradiation at 904 nm. The crosses indicate the increase of the $\chi_M T$ product with time upon irradiation of the sample. The occurrence of two steps thermal induced transition at well defined temperatures is evidenced in the inset, where $d(\chi_M T)/dT$ vs T is plotted.

Figure 2. View of the two crystallographically independent cationic units of **1**. Selected bond lengths [Å]: Co1–O1 1.873(11), Co1–O2 1.898(12), Co2–O4 1.869(11), Co2–O3 1.880(11) at 100 K; Co1–O1 1.986(12), Co1–O2 2.037(12), Co2–O3 1.883(12), Co2–O4 1.884(12) at 160 K.

acter of the conversion suggests the presence of two non-equivalent Co–diox molecules in the crystal lattice, whereas the absence of thermal hysteresis for both steps indicates a negligible cooperativity. It is interesting to note that the presence of toluene shifts down the transition temperature of about 200 K with respect to the ethanol solvate. This confirms the major role of the intermolecular interactions and crystal packing in determining the relative stability of the different charge distributions in valence tautomeric complexes.[17,18]

The presence of two distinct Co centers in the lattice is confirmed by the solution of X-ray structures at 100 and 160 K (Figure 2), even if we could only obtain a partial refinement[25] due to the probable formation of spin-like domains.[26] Notwithstanding these limitations, we can safely conclude that at both temperatures the asymmetric unit consists of two crystallographically independent [Co(Me₂tpa)-(DBdiox)]⁺ moieties, two (PF₆)⁻ anions and two toluene molecules. Most importantly, at 100 K the bond lengths characterising both cobalt ions indicate the same charge distribution (Co^{III}–Cat), whereas at 160 K they agree with the two molecules being in two different charge distributions, Co^{II}–SQ (Co1) and Co^{III}–Cat (Co2) (see caption to Figure 2).

The effect of the lattice-softening effect induced by toluene is also evident in the variation of the photomagnetic properties of the system. When irradiated at 904 nm and 9 K (ca. 1 mW cm⁻²), the system evolves to the metastable high-spin state, according to the valence tautomeric interconversion, Co^{III}–Cat → Co^{II}–SQ. Taking as a reference the 9 K $\chi_M T$ value of [Co(Me₃tpa)DBSQ]⁺[18] not undergoing VT, the steady-state conversion has been estimated to 85% of the total molar amount of cobalt after irradiation. Such a high percentage of conversion, compared with the ethanol solvate,[17,18] may be attributed to the increase of the lattice volume per molecule (3863 Å³ at 100 K for the toluene solvate vs 3799 Å³ at 150 K for the ethanol solvate). This may account by itself for the improved conversion capabilities of the cation, by reducing the lattice pressure. After switching
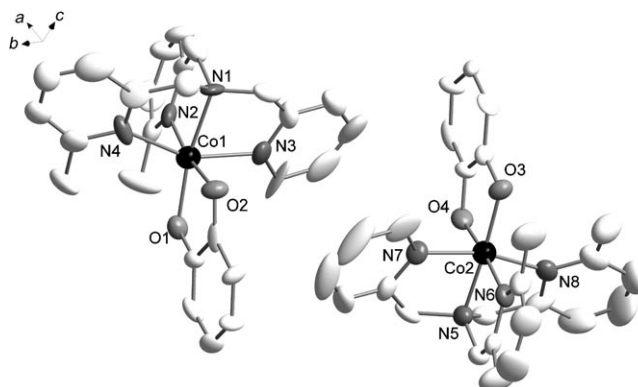
off the light and increasing the temperature, $\chi_M T$ recovered the pristine value around $T = 80$ K. The data suggest that the decay process does not occur in two well defined steps. The relaxation of the photoinduced high-spin metastable state has been monitored at different temperatures. The results obtained, normalized to the photoinduced fraction γ (Figure 3), were fitted using a stretched exponential law:[27]

$$\gamma(t) = \gamma(0)\exp(-t/\tau)^\beta$$

where the β parameter takes into account the time evolving crystal forces acting on a single reference molecule during the decay, due to the different molecular volumes of the high- and low-spin species, and τ is the relaxation time of the system at the temperature T.[28] This procedure gave for the lowest temperature a relaxation time of $1.18(\pm0.02)\times10^6$ s ($R^2 = 0.997$) which should be compared with $4.5(\pm0.1)\times10^5$ s obtained for the ethanolato derivative.[18]

Two distinct dependencies of τ with temperature were observed (Figure 3): in the high-temperature range (30–55 K) an Arrhenius behavior ($\tau(T) = \tau_0\exp(\Delta E/k_B T)$, in which τ_0 represents the pre-exponential factor and ΔE the energy barrier) with an energy barrier of $269(\pm27)$ cm⁻¹ and a pre-exponential factor of 4 (±1) s was obtained ($R^2 = 0.997$). The activation energy of the thermally induced relaxation agrees well with a mechanism involving the total-symmetric vibrational breathing mode of the Co–O bond, expected to be about 300 cm⁻¹. The comparison with previous results for ethanol solvate of **1** ($\Delta E = 242$ cm⁻¹, $\tau_0 = 4.5$ s)[17] points out the single-molecule nature of the LIESST phenomenon.[29] On the other side, the low temperature (9–20 K) behavior of the relaxation time exhibits a very weak dependence on temperature. A best fitting procedure with the Arrhenius relation gave $\Delta E = 1.3$ cm⁻¹ and $\tau_0 = 9.5\times10^5$ s, which is in agreement with a temperature independent tunneling of the system from the metastable high-spin state to the low-spin stable state at low temperature according to the Jortner theory.[30]
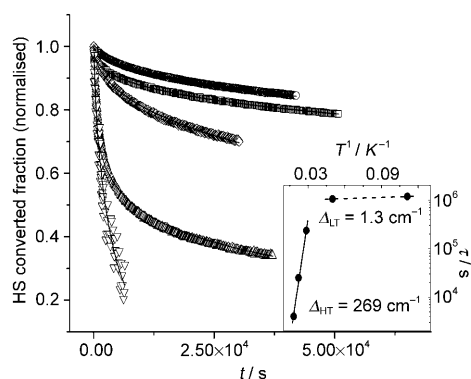
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Figure 3. Relaxation of the photoinduced fraction of **1** in the dark at 9 K (○), 20 K (□), 35 K (◇), 45 K (△), 55 K (▽) and best fits (continuous black lines) using the stretched exponential law with parameters reported in the text. The converted fraction is normalized at 1 when $t = 0$. Inset: the corresponding Arrhenius plot is reported, with two different regimes clearly distinguishable (dotted line for low temperature and continuous one for high temperature). The best fit lines are obtained using the parameters reported in the text.

Another important feature of this system is the possibility to enhance the rate of the relaxation process of the photoinduced metastable high-spin state by irradiation on its MLCT band located in the red region of the visible spectrum. This process, called reverse LIESST effect, discovered almost twenty years ago for spin-crossover compounds by Hauser,[31] took 16 years to be observed for a 1:2 Co/dioxolene based valence tautomer.[32] Its importance for a technological use of these compounds is obvious, candidating them as potential light triggered bistable switches or data storage media. Herein we report for the first time in a 1:1 Co–dioxolene species, which undergoes valence tautomerism. As shown in Figure 4, when the high-spin state is irradiated at 9 K with a 658 nm laser diode, its relaxation is much faster than in the dark. A stretched exponential fit gave a relaxation time of $1.58(\pm 0.04) \times 10^5$ s ($R^2 = 0.993$); this indicates that irradiation increases the relaxation rate of one order of magnitude ($\tau_{dark}(9\,\mathrm{K}) = 1.18 \times 10^6$ s). The possibility of this

being a thermal effect is ruled out by considering that the observed rate under irradiation at 9 K (power of ca. 1 mW cm^{-2}) is faster than that in the dark at 35 K (Figure 4). The reversibility of the process has been checked as well, assuring no degradation of the sample during several cycles of irradiation and relaxation.

In conclusion, we reported the effect of the change of recrystallisation solvent on the temperature and light dependence of the VT process of a 1:1 Co–dioxolene compound, showing a new way to tune its magnetic properties. In particular, the different dependence on the chemical surroundings of the thermal and light induced valence tautomeric transition paves the way for the development of new molecular magnetic materials with properties which may be controlled by chemical techniques.
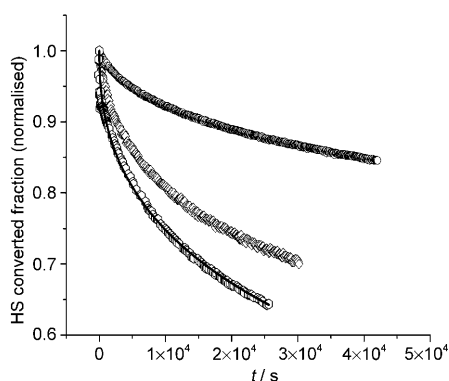
Figure 4. Comparison between the relaxation of the photoinduced fraction of **1** at 9 K in the dark (○) and under irradiation at 658 nm (○) and at 35 K in the dark (◇). The black solid line is the stretched exponential fit (parameters are given in the text).

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[25] The reason for the poor refinement[33a] should be ascribed to the occurrence of a third phase, most probably a fraction of the all Co^{II}–SQ phase nucleating at low temperatures. This could explain the presence of intense *h0l* reflections which should be extinct due to the glide plane of the space group $P2_1/c$. A refinement in the lower symmetry group $P2_1$ did not lead to an improvement of the quality, as in agreement with the *E* statistics of SIR-97,[33b] which clearly indicate that the structure is centrosymmetric. The probable presence of another phase is also suggested by different reflections at the end of the refinement, featuring high F_o and low F_c values. We are currently investigating this issue in more detail trying to assign a structure to this third phase.

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