Unprecedented optically induced long-lived intramolecular electron transfer in cobalt–dioxolene complexes†

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The observation of very long lifetimes of the metastable states of two cobalt–dioxolene complexes undergoing photoinduced and high T_c thermally-induced valence tautomer interconversion opens new research perspectives.

The discovery that irradiation of some iron(II) spin crossover complexes may induce interconversion from the diamagnetic low-spin state to the paramagnetic metastable high-spin one (LIESST effect) at cryogenic temperatures opened a challenging topic in material science for the potential exploitation of these compounds as molecular switches.[1–3] However, in order to have such application, it is required to reach a satisfactory comprehension of the factors affecting the lifetime of the photoinduced metastable species. It has been suggested that the low temperature relaxation decay of the optically induced high-spin state into the low-spin ground state occurs with a tunnelling mechanism and its rate increases exponentially with the energy difference between the ground vibrational levels of the two states, ΔE^0_{HL}. The observed experimental data have then been interpreted through the non-adiabatic multiphonon relaxation model developed by Hauser,[4,5] on the basis of the Jortner theory[6] for radiationless relaxation decay. In this framework, the key parameters that control the relaxation process are supposed to be ΔE^0_{HL} and Δr (*i.e.* the bond length difference between the two spin states). Following this theory, the highest ΔE^0_{HL} is associated with the fastest relaxation time. It was further suggested that ΔE^0_{HL} is inversely proportional to the critical temperature T_c (defined as the temperature at which the two species have equimolar abundance) characterising the thermally induced interconversion, thus allowing to develop a correlation between the relaxation rate and T_c (Inverse Energy Gap Law).[4,5]

Given its general formulation, this model may be extended to any molecular system showing interconversion between two vibronically coupled electronic states. For this reason it has been invoked for explaining the relaxation rates observed in cobalt–dioxolene complexes undergoing optically induced valence tautomeric interconversion.[7,8] This last process occurs as a result of an intramolecular electron transfer (ET) process between the coordinated dioxolene ligand and the metal ion.[8] In the simplest case[9,10] (*i.e.* a 1 : 1 cobalt–dioxolene complex) this is sketched by the following reaction scheme:

$$\mathrm{Co^{III}(L)Cat^+ \rightarrow Co^{II}(L)(SQ)^+} \quad (1)$$

where L is an ancillary ligand, Cat and SQ indicate the dioxolene ligand in its catecholato (diamagnetic) and semiquinonato (radical) form, respectively, while $\mathrm{Co^{III}}$ is in low spin (*ls*) and $\mathrm{Co^{II}}$ is in high-spin (*hs*) configuration. The process is then obviously characterised by a large variation of the magnetic properties of the system, since $\mathrm{Co^{III}}$–Cat is diamagnetic, whereas $\mathrm{Co^{II}}$–SQ is paramagnetic, and in a formal sense is similar to a spin crossover equilibrium.

Although pulsed laser photolysis studies inferred evidence that transient short lived $\mathrm{Co^{II}}$–SQ species could be generated by irradiating solutions containing the $\mathrm{Co^{III}}$–Cat ones,[7] it is only in the recent past that the possibility of photoinducing the ET process, yielding the *hs*-$\mathrm{Co^{II}}$ form as a long lived metastable species at cryongenic temperatures, has been established.[11–16] However the lifetimes of the metastable species were found to be shorter than those usually observed for $\mathrm{Fe^{II}}$ complexes exhibiting LIESST effect. This was believed to limit the potentiality of this class of molecules for their exploitation in information storage. In addition, the experimental activation energies controlling the temperature dependent decay rates were found to be significantly smaller than the ones expected on the basis of Hauser model.[17–19]

In order to obtain more detailed insight into the key parameters which determinine the relaxation rates of the photoinduced metastable states in cobalt–dioxolene valence tautomeric systems, we report here a complete analysis of the photomagnetic properties of two new such complexes, characterized by largely different T_c values.‡

The molecular structure of $\mathrm{[Co(Me_2tpa)(DBCat)]PF_6}$ ($\mathrm{Me_2tpa}$ = bis(6-methyl-(2-pyridylmethyl))(2-pyridylmethyl)amine, DBCat = 3,5-di-*tert*-butylcatecholato) is sketched in Fig. 1.§ The relevant bond distance lengths (Co1–O3 1.868(5) Å, Co1–O4, 1.880(5) Å, O3–C22 1.343(9) Å, O4–C21 1.348(8) Å, C21–C22 1.399(4) Å) are those characterizing the $\mathrm{Co^{III}}$–Cat charge distribution.[8] This is in agreement with the recently reported magnetic characterization of this system, which showed that it undergoes valence tautomeric interconversion with a T_c of 370 K.[20]

The irradiation of the sample with 904 nm wavelength at 9 K was found to induce a reversible partial conversion (estimated value: 3%) to the $\mathrm{Co^{II}}$–DBSQ species. As previously observed in similar systems, the low conversion percentage can be attributed to the strong opacity of the sample.

The relaxation kinetics of the metastable converted species were obtained by measuring the time dependence of the magnetization

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† Electronic supplementary information (ESI) available: χT *vs.* T curve for $\mathrm{[Co(Metpa)(Phencat)PF_6]}$. See DOI: 10.1039/b702932b

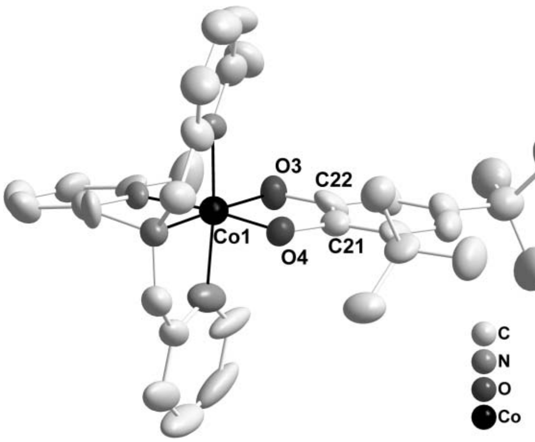

Fig. 1 Molecular structure of the cationic moiety of [Co(Me$_2$tpa)(DBCat)]PF$_6$. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are shown at 60% probability.

of the sample at different temperatures. The results are shown in Fig. 2. They were fitted assuming a first order stretched exponential decay according to the relationship:

$$\gamma(t)/\gamma_0 = \exp(-t/\tau)^{\beta} \qquad (2)$$

where $\gamma(t)$ is the converted molar fraction of the metastable state at the time t, γ_0 is the photoinduced molar fraction at $t = 0$, τ is the average relaxation time and β is a parameter comprised between 0 and 1, accounting for a time-evolving distribution of activation energies. The calculated average relaxation times τ were 4.5(1) × 10^5 s at 9 K, 3.0(1) × 10^5 s at 20 K, 1.9(5) × 10^5 s at 33 K, 8.7(6) × 10^4 s at 35 K, 3.8(2) × 10^4 s at 40 K and 5.6(4) × 10^3 s at 50 K, with β values ranging from 0.4 to 0.5.

As previously observed for other spin crossover and valence tautomeric interconversions,[4,17–19] the plot of $\ln(k) = \ln(\tau^{-1})$ *vs* $1/T$ evidences that the relaxation rate does not follow a simple Arrhenius law, as expected for a single thermally activated process. We found two thermally activated relaxation regimes characterised by very different parameters, one between 5 and 20 K, and another one at higher temperatures (35–50 K). A tentative fit to the Arrhenius law ($\tau = \tau_0\exp(-E_a/k_BT)$, where τ_0 is the relaxation time at infinite temperature and E_a is the activation barrier for the relaxation, gives in the low temperature region τ_0 = 5 × 10^5 s and E_a = 9 cm^{-1}, and in the high temperature region τ_0 = 4.5 s and E_a = 242 cm^{-1}. The low E_a value obtained for the low temperature relaxation data suggests that a lattice-phonon assisted tunneling mechanism is operative in this region.[18] On the other hand, the observed E_a value relative to the high temperature region well agrees with the energy associated to the total-symmetric Co–O vibrational breathing mode, which is expected to be of the order of 300 cm^{-1}. As this breathing mode is expected to coincide with the zero point energy difference, $\Delta E_{HL}{}^0$, the observed behaviour is well consistent with the Hauser model based on the Jortner theory. We however stress that the observed T_c for this complex is significantly higher than the one observed for [Co(CTH)(PhenCat)]PF$_6$ complex (about 300 K),[21] while the lifetime of the photoinduced metastable state is about twenty times longer (4.5 × 10^5 s *vs.* 2.0 × 10^4 s at 10 K). This is contrasting with the expectation of a parallelism between the decay rate constant of the photoinduced species and the T_c of the thermally induced (entropy driven) interconversion.

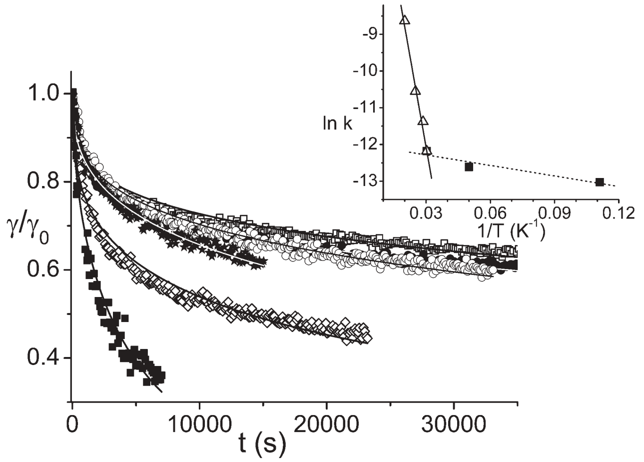

Fig. 2 Time evolution of the metastable photoinduced fraction of Co(Me$_2$tpa)(DBCat)PF$_6$ at 9 K(empty squares), 20 K(full circles), 33 K(empty circles), 35 K(stars), 40 K(rhombi) and 50 K(full squares) and corresponding best fit parameters. In the inset it is reported the corresponding Arrhenius plot, with two different regimes clearly distinguishable. See text for best fit parameters.

At first glance one might attribute this discrepancy to the differences in the coordination sphere and in the radical ligand employed. To further investigate this issue, we have then analyzed the kinetic parameters characterizing the relaxation decay of the paramagnetic species generated by photoirradiation of the [Co(Metpa)(Phencat)]PF$_6$ complex (Metpa = bis(2-pyridylmethyl)(6-methyl-2-pyridylmethyl)amine), which is expected to show increased analogy with [Co(CTH)(PhenCat)]PF$_6$. Unfortunately, repeated attempts of obtaining suitable crystals to be used for diffractometric analysis failed. This system has been found to be diamagnetic in the 4–310 K temperature range.† Therefore, the critical temperature T_c of a possible valence tautomeric interconversion process is expected to be much higher than the one observed for [Co(Me$_2$tpa)(DBCat)]PF$_6$.¶

In this case, the irradiation at 9 K with a continuous laser beam at 904 nm was found to induce a reversible partial conversion (estimated value: 14%) to the Co^{II}–PhenSQ species. The relaxation kinetics at various temperatures of the photoinduced metastable species are shown in Fig. 3. The calculated average relaxation times were 8.2(1) × 10^6 s at 9 K, 2.2(2) × 10^6 s at 20 K, 1.0(1) × 10^6 s at 35 K, 1.7(1) × 10^5 s at 42 K, 4.9(8) × 10^4 s at 50 K and 5.4(5) × 10^3 s at 65 K, with β values ranging again from 0.4 to 0.5.

The corresponding Arrhenius plot is shown in the inset of Fig. 3. Again, two thermally activated relaxation regimes are observed. The one occurring between 9 and 35 K is characterised by a τ_0 = 6.3 × 10^5 s and E_a = 14 cm^{-1}, whereas the second regime occurs between 35 and 65 K and is characterised by τ_0 = 12 s and E_a = 295 cm^{-1}. These data support the conclusions we suggested above and are fully consistent with the Hauser model. However, the comparison of these data with those of [Co(CTH)(PhenCat)]PF$_6$ and of [Co(Me$_2$tpa)(DBCat)]PF$_6$, clearly evidences the absence of any correlation between the relaxation rates of the photoinduced states and the T_c of the entropy driven interconversion. Since this parallelism suggested by Hauser finds its origin in the assumption of a negligible variation of the entropic term in spin crossover

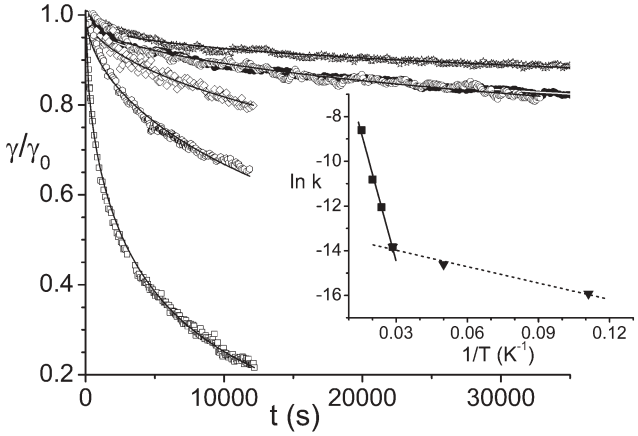

Fig. 3 Time evolution of the metastable photoinduced fraction of $[Co(Metpa)(PhenCat)]PF_6$ at 9 K (stars), 20 K (full circles), 35 K (empty circles), 42 K (rhombi), 50 K (hexagons), 65 K (squares) and corresponding best fit curves. In the inset it is reported the corresponding Arrhenius plot, with two different regimes clearly distinguishable. See text for best fit parameters.

complexes, we may conclude that this assumption is not at all satisfied in valence tautomeric complexes, even when analysing homologous series of complexes.[4] It is then reasonable to think that the model should be implemented with the introduction of other physical parameters to account for the specific case of cobalt-dioxolene systems. Finally, we stress here the large values of the lifetime of the photoinduced paramagnetic metastable phase. They are the longest ones observed up to date for photoinduced cobalt-dioxolene valence tautomeric complexes. We think that these results clearly widen the intrinsic technological perspective associated to the development of this research topic.

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Notes and references

‡ Experimental details: Metpa and Me_2tpa ligands were synthesised according to literature methods.[22] The complexes were obtained by mixing methanol solutions containing cobalt chloride and the ligand in 1 : 1 ratio with a solution of the appropriate catecholate and triethylamine (1 : 2.5 ratio) in the same solvent under inert atmosphere. The metal(II)–catecholato complexes were oxidised with atmospheric dioxygen and the resulting products were precipitated by adding an aqueous solution of KPF_6. Physical Measurements: the photomagnetic characterisation of the samples was performed with the irradiation of thin pellets (2–3 mg) of polycrystalline powder. The experiments were performed by a S600 Cryogenic SQUID Magnetometer equipped with an optical fiber and a specifically designed sample holder. Earlier calibration of the setup was accomplished to remove any stray contributions due to the arrangement.[18] Both $[Co(Metpa)(PhenCat)]PF_6$ and $[Co(Me_2tpa)(DBCat)]PF_6$ derivatives were irradiated at 9 K using 904 nm CW laser light up to 10 mW cm^{-2} output power. The percentage of photoconversion was evaluated measuring the χT value at 9 K for the compounds before and after irradiation. It was estimated as 3% and 14% respectively for the $[Co(Me_2tpa)(DBCat)]PF_6$ and the $[Co(Metpa)(PhenCat)]PF_6$ derivatives at the photostationary limit, which was reached for both the compounds after 5 h of continuous irradiation at 9 K. Subsequent tests performed by varying the output laser power from 1 up to 10 mW cm^{-2}, showed that no effect of the increased power was observed on the conversion percentage at the equilibrium. The converted fraction was evaluated according to $(\chi T(t = 0) - \chi T_{OFF})/(\chi T_{Co(II)-SQ} - \chi T_{OFF})$ where $t = 0$ is the initial time relative to the relaxation decay and χT_{OFF} is the value for the non-irradiated compound. The $\chi T_{Co(II)-SQ}$ values for the Co(II)–SQ species were taken as 2.44 emu K mol^{-1} and 2.0 emu K mol^{-1} respectively for the $[Co^{II}(Me_2tpa)(DBSQ)]PF_6$ and the $[Co^{II}(Metpa)(PhenSQ)]PF_6$ derivatives. These quantities were derived from $[Co^{II}(Me_3tpa)(DBSQ)]PF_6$ and $[Co^{II}(Me_2tpa)(PhenSQ)]PF_6$ compounds present as Co^{II}–SQ in the 4–300 K temperature range. The low conversion factor can probably be ascribed to the strong opacity of the samples that prevents the penetration of light in the deep layers, as observed also for similar systems. The low percentages of conversion then just reflect the small absolute quantity of molecules of the sample in the surface layers. The relaxation kinetics were recorded switching off the laser light as soon as the photostationary limit was achieved. For kinetic measurements performed at T greater than 9 K, the laser diode was switched off after the sample was thermalised at the selected temperature. For all the measurements, the reversibility was tested increasing the temperature at a certain value to allow the full relaxation of the photoinduced metastable fraction and afterwards, thermalising again at 9 K. For the $[Co(Me_2tpa)(DBCat)]PF_6$ derivative, heating the sample up to 80 K was sufficient, whereas the $[Co(Metpa)(PhenCat)]PF_6$ derivative required temperatures up to 100 K. This test can be considered analogous to the T_{LIESST} measurement and the results found are in agreement with the greater 'renitency' of the metastable fraction of the $[Co(Metpa)(PhenCat)]PF_6$ derivative with respect to the $[Co(Me_2tpa)(DBCat)]PF_6$ one.

§ Crystal data for $[Co(Me_2tpa)(DBCat)]PF_6 \cdot 1.25C_2H_5OH$ M = 800.2(1), monoclinic, space group $P2_1/n$, a = 12.944(4), b = 16.805(5), c = 17.746(5) Å, β = 100.17(3)°, V = 3800(2) $Å^3$, T = 150(2) K, Z = 4, $\mu(\lambda$ = 0.71073 Å) = 0.565 mm^{-1}, ρ_{calcd} = 1.399 Mg m^{-3}, 9697 reflections measured, 4414 unique, and 2401 ($I > 2\sigma(I)$) used in the calculations; $R1$ = 0.0788, w$R2$ = 0.1906. The solvent molecule with partial occupation was found to be disordered over two symmetry related sites. CCDC 638171. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b702932b

¶ We note here that the occurrence of valence tautomerism at higher temperatures is very plausible since the existence of $Co(Metpa)(Phendiox)^+$ in the form of the $Co^{II}(Metpa)(PhenSQ)^+$ redox isomer is observed in solution at room temperature.

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