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Controlled light and temperature induced valence tautomerism in a Cobalt-o-Dioxolene complex

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ABSTRACT

The mononuclear cobalt complex of 3,5-di-tert-butylcathecolate and cyan-pyridine is a very versatile compound that displays valence tautomerism (VT) in the solid-state which is induced by temperature, light and hard X-rays and modulated by solvent in the crystal lattice. Here, we demonstrate the photo-induced valence tautomerism in benzene solvated crystals of such complex with a very high yield of metastable states using 450nm light, and also show evidence of the de-excitation of these photo-induced metastable states using red 660nm light. In our work we use single crystal X-ray diffraction as a probe for the VT and demonstrate the controlled use of hard X-rays using attenuated X-ray beams in order to control the X-ray induced VT interconversion. Our results point to a larger efficiency in the VT interconversion when *d-d* transitions are excited in comparison with charge transfer promotion.

KEYWORDS. Valence tautomerism, single crystal X-ray diffraction, Cobalt o-semiquinone.

1. INTRODUCTION

Smart materials are those designed to respond to mechanical, chemical, electric or magnetic stimuli from the surrounding environment having one or more of their properties significantly changed in a controlled manner. Among these materials, those that present electronic bistability in the form of spin-crossover[1] (SC) or valence tautomerism[2] (VT) can be used potentially as sensors, signal processors and information storage devices for they can readily switch between two spin and/or electronic states[3–5]. Of particular interest are the solid-state materials composed by molecules that present valence tautomerism at a single metal center or within a molecular complex without substantial disruption of the solid-state structure[6,7].

Generally, the investigation of materials presenting VT is focused on the metal ions and the associated ligands that act as charge donors. In such materials, the VT process is accompanied by changes in structural, electronic and thermodynamic properties, and can therefore be characterized with a number of experimental approaches and theoretical calculations. Of particular significance is the understanding of the effects of the variation of external factors on the VT properties and dynamics. It has been established that the symmetry of the environment, the nature of the ligands associated with the metal center, the presence and nature of solvate molecules and counter ions [7–11], as well as temperature[12], pressure[13], illumination[5], magnetic and electric fields [14] and irradiation [5,15,16] will greatly impact the VT. The yield and rate of intramolecular electron transfer, the lifetime of induced metastable states and the stability of high-spin (hs) and low spin (ls) states are some of the important properties that can be modulated and controlled by external stimuli.

Complexes that display VT are composed by a transition metal ion center, organic redox-active ligands that act as charge donors and organic ancillary ligands. Such complexes can form continuous solids in which intermolecular interactions extend over the lattice in one, two or three dimensions. Of the materials that present VT in the solid-state, the family of complexes with a cobalt metal center, dioxolene molecules that act as redox-active ligands and nitrogen based ancillary ligands have been thoroughly studied in the last decade[7]. These compounds undergo the reversible valence and spin interconversion from *ls*-$Co^{III}(SQ)(Cat)R$ to *hs*-$Co^{II}(SQ)_2R$ (*ls*: low spin, *hs*: high-spin; SQ: semiquinone; Cat: catecholate; R: 2 monodentate or 1 bidentate nitrogen based ligand). The interconversion is accompanied by a couple of reversible structural changes[9,16] that reflect the change of the electronic population of the metal and ligand orbitals. In particular, the isotropic contraction/expansion of the Co–L (L=O1, O2, N1 atoms) coordination sphere has been shown to be systematic in such a way that the interatomic distances between the Cobalt atom and its first neighboring atoms (the O atoms from the dioxolene and the N atoms from the ancillary ligand) can be used to compute the molar fraction of *hs*-Co^{II} and *ls*-Co^{III} within a crystal. Alternatively, the distances between the atoms of the redox-active ligand can be used to compute the empirical “metrical oxidation state" (MOS), which gives a continuous measure of the apparent oxidation state of the ligand[17]. The values of all atomic distances within the complexes can be easily accessed through single crystal X-ray diffraction experiments.

Within the family of cobalt complexes that present VT, the octahedral cobalt with two 4-cyan-pyridine (4-CN-py) molecules as ancillary ligands and two 3,5-di-tert-butyl-semiquinonate/catecholate (3,5-DBSQ / 3,5-DBCat) as redox active ligands in trans configuration is a very versatile compound ($Co^{III}(diox)_2(4\text{-CN-py})_2$ from here on). Its valence tautomerism has been shown to be controllable, being induced by temperature[12], visible light irradiation[18] and hard X-rays[16], and modulated by the absence or presence of solvent in the crystal lattice[8,9]. This complex was demonstrated to behave similarly to light-induced excited state spin trapping (LIESST) complexes for its highly stable photogenerated Co^{II} form at temperatures lower than 50K[18]. The stability of such excited states is believed to be due to lattice stabilization through hydrogen bonds[9]. However, the photo-conversion induced by white light was shown to be inefficient (30% yield), even though the wide spectrum of the white light seemed to have allowed for a higher interconversion rate by comparison to monochromatic laser illumination[18]. The electronic absorption spectrum of the ($Co^{III}(diox)_2(4\text{-CN-py})_2$) in solution has also been reported[18], and its ligand to metal charge transfer (LMCT) band is centered approximately at 740nm ($13500cm^{-1}$) and ranges from 500nm to 1000nm ($20000cm^{-1}$ to $10000cm^{-1}$). On the other hand, the $Co^{II}(diox)_2$ species with different ancillary ligands have been shown to display internal ligand transition bands near 800 nm (12500 cm^{-1}) and charge transfer transitions between 525-665nm (15000-19000 cm^{-1})[6,19,20]. Subsequent research showed that the photo-interconversion yield can be as high as 100% when the sample is irradiated with hard X-rays (25.5keV)[16]. The underlying process, named hard-X-ray-induced excited-spin-state trapping (HAXIESST), and the electronic dynamics involved is not yet understood~~.~~

In the present work, we continue to investigate the VT interconversion in (Co(*diox*)$_2$(4-CN-py)$_2$), where *diox* is 3,5-DBSQ/3,5-DBCat, and we demonstrate the photogeneration of metastable Co^{II} centers from Co^{III} centers at 30K with 80% yield for a benzene solvated single crystal using 450nm blue light (22222 cm^{-1}). We also present evidence for the reverse de-excitation using 660nm red light (15151.5 cm^{-1}).

2. EXPERIMENTAL SECTION

2.1 Crystallization

The synthesis of [Co^{III}(SQ)(Cat)(4-CN-py)$_2$] (SQ: 3,5-di-tert-butyl-o-semiquinonate, Cat: 3,5-di-tert-butyl-o-cathecolate, CN-Py: cyano-pyridine) followed the procedures reported previously[18]. Benzene solvated crystals were grown by slow evaporation of benzene under a N_2 atmosphere[9]. The procedures afforded dark blue needle crystals suitable for X-ray diffraction experiments.

2.2 Single crystal X-ray diffraction data collection

The benzene solvated crystals were submitted to single crystal X-ray diffraction (SCXRD) experiments at the I19-2 beamline of the Diamond Light Source (Oxfordshire, UK), using 25.5keV X-rays and multiple attenuation values for the 200µm x 200µm beam. Samples were manually mounted on MiTeGen UV mounts in copper magnetic bases. Light-induced VT was probed in samples kept at 30K; temperature-induced VT was probed from 30K to 300K. All low temperature SCXRD measurements had samples cooled using an open flow He cryostat (nHeliX, Oxford Cryosystems). Sample illumination was achieved using blue (450nm) and red (660nm) light from laser diodes (L450P1600MM and L660P120, ThorLabs, see Table S6 and Figure S8 of the supplementary information). Homogenous illumination of the samples was possible using an in-house illumination ring that was placed around the low temperature device nozzle. The hutch lights were kept off for all the experiments, and during the SCXRD experiments, the diodes were turned off.

SCXRD data processing was performed using XDS[21], structure solution and structure refinement using SHELXT[22] and SHELXL[23] respectively, with the aid of python scripts (available upon request) that automatically run XDS and SHELXL sequentially for all datasets. The retrieval and analysis of quality indicators of data processing and refinement were also made using python scripts.

2.2 *hs*-Co^{II} molar fraction calculation

The molar fraction of the cobalt centers with different oxidation states were computed following the equations proposed by Ribeiro et al[9].

$$\gamma(hs - Co^{II})_L = (D_{exp}^{Co-L} - D_{Co^{III}}^{Co-L})/(D_{Co^{II}}^{Co-L} - D_{Co^{III}}^{Co-L}) \qquad (1)$$

$$\gamma(hs - Co^{II}) = \frac{1}{3}\sum_L \gamma(hs - Co^{II})_L \qquad (2)$$

Where L denotes the atoms in the first co-ordination sphere of the cobalt center, $D^{Co\text{-}L}$ stands for the atomic distance between Co and L and the subscripts denote the experimental value (exp) and the standard distances for both oxidation states of Co (Co^{II} and Co^{III}) averaged from distances surveyed in the Cambridge Structural Database (CSD)[24] and indicated in Table 1. The error for the calculated values of *hs*-Co^{II} was evaluated by the partial derivatives method.

Table 1. Reference Co-N and Co-O distances surveyed from CIF files1559584−1559598 at the CCDC databank.

$D_{\mathrm{Co}^{III}}^{\mathrm{Co-N}} = 1.940(16)$Å	$D_{\mathrm{Co}^{II}}^{\mathrm{Co-N}} = 2.151(7)$Å
$D_{\mathrm{Co}^{III}}^{\mathrm{Co-O1}} = 1.889(6)$Å	$D_{\mathrm{Co}^{II}}^{\mathrm{Co-O1}} = 2.060(5)$Å
$D_{\mathrm{Co}^{III}}^{\mathrm{Co-O2}} = 1.872(12)$Å	$D_{\mathrm{Co}^{II}}^{\mathrm{Co-O2}} = 2.045(2)$Å

The MOS for the redox-active ligand was also computed using the method developed by Brown, 2012[17] (Section 3, supplementary information).

SCXRD data and structure refinement statistics for all the crystals used in this work at 30 K are reported in Table S2 of the supplementary information. I/sigma, cc1/2 and r1 parameters evolution for each experiment as a function of temperature and irradiation time are reported in Figures S1, S2 and S3 of the supplementary information.

3. RESULTS AND DISCUSSION

3.1 Structure description

The (Co(*diox*)$_2$(4-CN-py)$_2$·benzene crystallizes in the monoclinic space group $P2_1/c$, with two (Co*(diox)*$_2$(4-CN-py)$_2$) molecules in the unit cell (Z=2). The Co atom sits on a crystallographic center of symmetry, with one *diox*, one 4-CN-py ligand and one benzene solvent molecule in the asymmetric unit. Because of the symmetry requirement there is only one unique *diox* ligand so that in the high-spin state of the complex the resultant $SQ^{\bullet-}$ and/or Cat^{2-} forms are superimposed. Therefore, X-ray diffraction technique affords only an average of the $SQ^{\bullet-}$ and/or Cat^{2-} forms in the *ls*-[$Co^{3+}(SQ^{\bullet-})(Cat^{2-})$] isomer. Figure 1 shows the molecular structure of the complex in a benzene solvated crystal at 30 K, solved by single crystal X-ray diffraction (SCXRD).

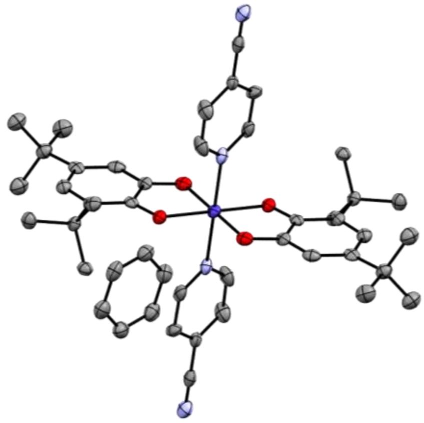

Figure 1. Molecular structure of benzene solvated (Co(*diox*)$_2$(4-CN-py)$_2$) crystal at 30K. Atom colors: Co (dark blue), C (gray) N (light blue), O (red). Hydrogens are hidden for clarity purposes.

3.2 X-ray induced VT

The valence tautomeric interconversion of [Co(*diox*)$_2$(4-CN-py)$_2$] can be induced by X-ray irradiation of the benzene solvated crystals at low temperatures, though the yield of *hs*-Co^{II}

photogeneration has been shown to be highly dependent on the incident X-ray flux[16]. This property has to be observed and controlled in order assure minimal interference of the X-ray irradiation when probing the VT induced by visible light illumination in SCXRD experiments. Initial SCXRD experiments were then used to probe the electronic state of the metallic center when the crystals were under hard X-ray (25.5keV) irradiation. The estimation of the molar fraction $\gamma(hs - Co^{II})$ of hs-Co^{II} states within the crystal was done based on the Co-L distances (L = O1, O2 and N) using the method proposed by Ribeiro et al.[9] (equations 1 and 2).

The evaluation of the molar fraction of X-ray induced hs-Co^{II} in the crystal as a function of X-ray exposure time was achieved with multiple sequential SCXRD measurements performed on the same crystal at 30K for 0.25 and 0.6 transmission (runs 1,2,3,4,5 and 6,7 respectively, see Table S1 of the supplementary information) of the X-ray beam. SCXRD datasets were acquired sequentially except for the fifth dataset obtained after 30 minutes of irradiation by the non-attenuated X-ray beam (Figure 2). No rotation of the crystal was performed when full transmission of the beam was used, leading to a lower X-ray induced VT interconversion when compared to the rotating sample exposed to 0.25 and 0.6 beam transmission. The crystal information and crystallographic quality indicators of these experiments are shown in Table S1 of the supplementary information.

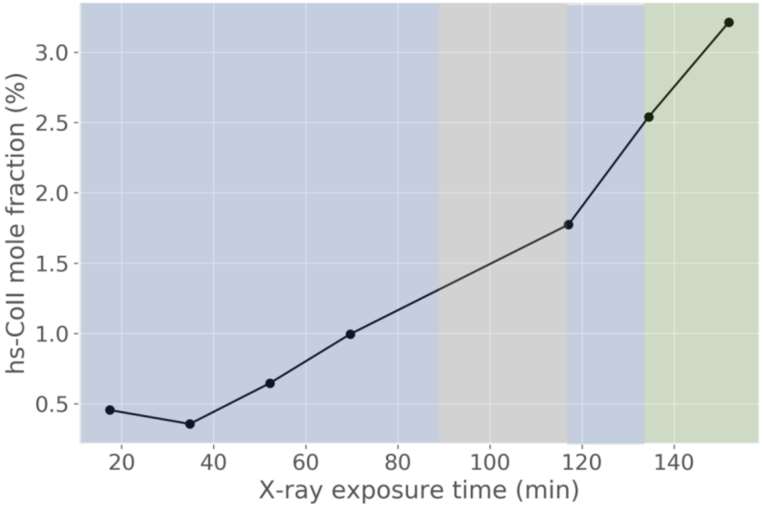

Figure 2. Molar fraction of hs-CoII species induced by X-ray irradiation during SCXRD experiments with the [$Co^{III}(diox)_2(4\text{-CN-py})_2$]·benzene crystal at 30 K. The blue, grey and green shaded regions correspond respectively to time intervals in which the crystal was exposed to 0.25, 1 and 0.6 transmission of the X-ray beam.

Figure 2 shows the calculated Co^{II} molar fraction as a function of X-ray irradiation time. The results revealed that for that specific beamline and for a crystal with dimensions of 100μm x 50μm x 50μm, the hs-Co^{II} molar fraction induced by X-ray irradiation was smaller than 3%, even for full beam transmission. In the experiments 6 and 7 the molar fraction of metastable hs-Co^{II} seems to grow faster than in the 5 previous experiments and this is likely to be due to the exposition to high X-ray intensity during the SCXRD data collection. Nevertheless, only 3% of metastable molar fraction was induced after all the 140min of hard X-rays irradiation. The average error for the calculated molar fraction was calculated to be 4%, which is already larger than the values observed. Using a conservative approach for subsequent experiments, the attenuation of the X-ray beam was chosen to ensure negligible X-ray VT conversion, in which $\gamma(hs - Co^{II})$ is smaller than 1% after 60 min of X-ray exposure. As expected, the calculated MOS of the dioxolene ligands corroborate with the change in the oxidation state of the metal calculated solely by metal-O/N interatomic distances (Figure S5).

3.3 Blue light induced VT

Crystals of the non-solvated $Co(diox)_2(4\text{-CN-py})_2$ have also been shown to display light induced valence-tautomerism VT by Schmidt *et al.*[18]. In that work, samples were kept at 10 K and illuminated with white light (from 450nm to 850nm, no spectrum shape is reported) and the presence of hs-Co^{II} was monitored through magnetic susceptibility measurements. A photo-stationary limit for the metastable hs-Co^{II} redox isomer conversion was never achieved, as the value of the magnetic susceptibility continued to grow (albeit at a very slow rate) even after

12*h* of illumination, with maximum conversion percentages approaching 30%. Later, Francisco et al. showed that 100% conversion to the metastable *hs*-Co^{2+} form at 30 K in solvated crystals is possible using non-attenuated hard X-rays, without any disruption of the crystal lattice or loss in crystal quality after recuperation of initial states[16]. This last result proved that the crystal lattice does allow for the full VT interconversion. Moreover, it is known that the VT interconversion for certain complexes can be induced both ways, from *ls*-Co^{III} to *hs*-Co^{II} and vice versa, using different excitation and de-excitation wavelengths[9]. Therefore, it could be that for the $Co(diox)_2(4\text{-CN-py})_2$ crystal, in the work of Schmidt *et al.*, both excitation and de-excitation wavelengths are contained within the wide spectrum used, and concomitant excitation de-excitation processes limited the VT interconversion rate [18]. To test such hypothesis, in this work, a benzene solvated crystal with dimensions of 300μm x 100μm x 100μm was mounted, cooled down to 30K, and illuminated with blue 450nm laser diode light (28.84mA) while being rotated with respect to the diode array using the goniometer. SCXRD datasets were acquired with 5% transmission of X-rays for 0, 5, 35, 55 and 75 min of LED illumination. The respective crystal structures were solved and the metastable *hs*-Co^{II} molar fractions were calculated. Figure 3 shows that after 55min of light illumination, an 80% metastable *hs*-Co^{II} conversion yield plateau is reached. This limit could be related to the penetration depth of the blue light through the crystal. Moreover, the electronic absorption spectrum of the $Co^{III}(diox)_2(4\text{-CN-py})_2$ complex in solution[12] was shown to have its charge transfer (CT) band ranging from 500 nm to 1000 nm (20000 cm^{-1} to 10000 cm^{-1}) and centered at approximately at 740 nm (13500 cm^{-1}). The 450 nm (22222 cm^{-1}) blue light used herein lies in a low absorption cross section region of the electronic absorption spectrum and has been assigned to *d-d* transitions[20,25–30]. Yet, wavelengths lying in the edge of the MLCT band for ls-CoIII (<500 nm) have also been reported to induce the VT in electronic processes involving charge transfer and intersystem crossing[29,30]. In our experiments, the 450 nm irradiation leads to the largest (~80%) yield photo induced VT interconversion ever observed in Co(*diox*)$_2$(4-CN-py)$_2$ compounds.

After the plateau was reached, the illumination was turned off and a temperature dependent sequence of SCXRD experiments shows the full recovery of *ls*-Co^{III} states (approximately 0% *hs*-Co^{II} molar fraction between 55K and 90K) and the subsequent well-known second-order (non-cooperative) VT interconversion in the characteristic temperature range of 150-230K. At 300K, 100% of the unit cells have units of the complex in the hs-Co^{II} state. After reaching room temperature, the crystal was again cooled down to 30K, and the SCXRD shows that the quality of the crystal is also recovered after all the interconversion cycles (Table S2, run 21). As expected, the calculated MOS of the dioxolene ligands corroborate with the change in the oxidation state of the metal calculated solely by metal-O/N interatomic distances (Figure S6).

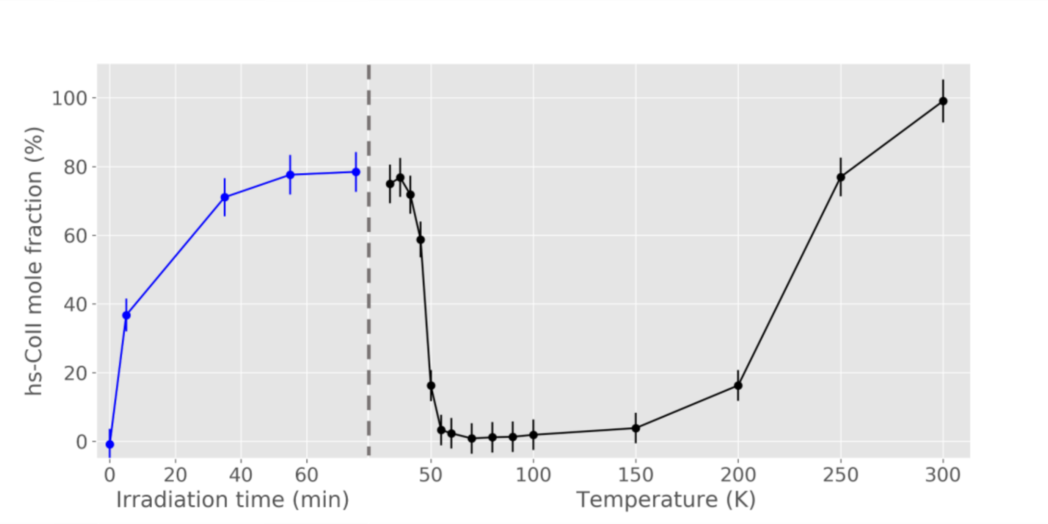

Figure 3. Molar fraction of *hs*-Co^{II} species in the [Co^{III}(*diox*)$_2$(4-CN-py)$_2$)]·benzene crystal when exposed to blue 450 nm illumination (blue points) at 30 K and to an increase in temperature from 30 to 300 K (black points).

The evolution of the data statistics and structural refinements quality indictors as a function of light illumination time and temperature indicates that the illumination does no more damage to the crystal than the increase in temperature (Figure S1), demonstrating the robustness of such material as a solid-state tautomer.

3.4 Red light induced VT

The high photoconversion yield of blue light illumination observed in our experiment reinforces the belief that the broad white light spectrum used by Schmidt *et al.*[18] also contains the metastable state de-excitation wavelengths, limiting the observed interconversion yield. To test the hypothesis, a 660nm laser diode was used to illuminate another benzene solvated crystal (80μm x 40μm x 40μm) of Co(*diox*)$_2$(4-CN-py)$_2$ at 30K, which was submitted first to blue 450nm light irradiation to achieve the high-spin states and to SCXRD experiments with 40% X-ray transmission. The higher transmission was necessary for sharper and more intense SCXRD images, because the crystal was substantially smaller than the ones previously used. Initially, sequential dark measurements were taken to establish the baseline for the X-ray induced interconversion. After that, the blue 450nm laser diode was turned on and used to illuminate the rotating sample. SCXRD experiments were performed after set intervals of light irradiation (5, 10 and 30 min). Two datasets were sequentially collected after 30min of blue light irradiation, and immediately after that, the red 660nm laser diode was turned on to irradiate the rotating crystal. The SCXRD datasets were acquired after 5, 10 and 20 minutes of red-light irradiation.

The calculated *hs*-Co^{II} molar fraction for the resolved Co(*diox*)$_2$(4-CN-py)$_2$ crystal structure under illumination in the described experimental sequence is shown in Figure 4. The X-rays induced around 16.22%±0.05% of metastable *hs*-Co^{II} even before the blue 450nm irradiation, though the blue light lifted the interconversion yield to 90.60%±0.05% after 30min of irradiation. The subsequent, partial de-excitation of the complexes is observed when the crystal is irradiated with the red 660nm diode. A decrease in the *hs*-Co^{II} molar fraction is observed until it reaches a plateau of 72.12%±0.05%.

The 660 nm (15151 cm^{-1}) light lies on the charge transfer band region of the electronic spectra of Co^{II}(*diox*)$_2$ complexes[12,19,20,26,29,31], and would be expected to induce the charge transfer. However, its lower efficiency in inducing the VT could indicate that the penetration depth of such wavelength may be a limiting factor. It is important to note that many effects are being considered: the VT induced by the X-rays irradiation, the stability of the photo-excited states from the blue light and the back valence-tautomerism observed after illumination with 660 nm red light. The crystals are only being exposed to X-rays during the SCXRD experiments, which last for 4.35 min (0.4s per image, 653 images per run – see Table S1 of the supplementary information) and the metastable *hs*-Co^{II} states are spin trapped at 30 K. The observed decay can only be due to the red 660 nm illumination, which is demonstrated to be more than sufficient to counterbalance the X-ray excitation. As expected, the calculated MOS of the dioxolene ligands corroborate with the change in the oxidation state of the metal calculated solely by metal-O/N interatomic distances (Figure S7).

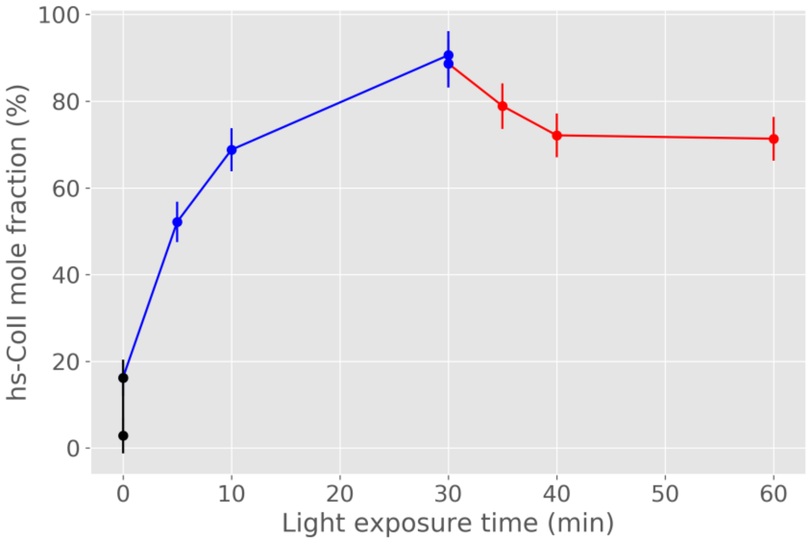

Figure 4. Molar fraction of *hs*-Co^{II} species induced by X-rays (black dots), blue 450 nm light (blue dots) and red 660 nm light (red dots) as a function of irradiation time for the the [Co^{III}(*diox*)$_2$(4-CN-py)$_2$)]·benzene crystal at 30 K.

The penetration depth issue for all the light radiation used in our experiments still remain unsolved, as we were not able to characterize it, or characterize the dependence of the VT interconversion yields to the crystal size. If it is the case of the penetration of red 660nm light is too small, the back VT will be severely limited.

4. CONCLUSIONS

In our work we presented the light-induced VT with high yield of metastable states of the benzene solvated [Co(*diox*)$_2$(4-CN-py)$_2$] crystal. The versatility of the tautomer studied here brings about a series of questions on the mechanisms of the tautomeric interconversion displayed by this material. Because of the very different nature of the visible white light and the hard X-rays used to induce the VT, along with their respective interconversion yields, it is plausible that they induce VT via different processes.

Despite the previously reported capability of hard X-rays to induce the VT interconversion[16], we demonstrated that the effect of the X-rays can be reduced and nearly eliminated by attenuating the X-ray beam to an appropriate flux. Therefore, the VT interconversion was successfully probed using single crystal X-ray diffraction at a synchrotron source with an attenuated X-ray beam where the X-rays were not inducing the formation of metastable states.

Our results show that the *ls*-Co^{III} $\Leftrightarrow$ *hs*-Co^{II} transition in the benzene solvated [Co(*diox*)$_2$(4-CN-py)$_2$] crystals, when induced either by X-rays, light or temperature, is reversible. Most importantly, we have shown that the *hs*-Co^{II} metastable state can be photo-induced in benzene solvated [Co(*diox*)$_2$(4-CN-py)$_2$] single crystals when illuminated with 450nm blue light at 30K with a very high interconversion yield (80%) and relaxed back to the *ls*-Co^{III} state when illuminated with a 660nm red light. However, the latter has a much smaller yield. Illumination with wavelengths lying in the edge of the charge transfer band for *ls*-Co^{III} (< 500 nm) have been reported to induce the VT in Cobalt dioxolane complexes. Numerous attempts to probe the ultrafast electronic dynamics involved, as well as the exact energy assignment of molecular orbitals in the *ls*-Co^{III} and *hs*-Co^{II} species have been performed and the VT process has been shown to be composed of a chain of events, spanning from charge transfer, spin crossover and vibrational relaxations. Thus, the reorganization of d electrons that can be promoted by d-d transitions may as well trigger a chain of events that lead to charge transfer.

The high yield light-induced metastable state generation reported for the 450 nm light irradiation had never been experimentally observed in molecular crystals of cobalt dioxolane tautomers. Such result, along with the light-induced back-valence tautomerism, evidenced the complexity of electronic events comprised in the valence tautomerism interconversion and call for a deeper study of the electronic dynamics of the light induced VT in transition metal complexes. In fact, the understanding of complex cascade of electronic events that may take place require time dependent DFT calculations (not yet reported in the literature, to the best of our knowledge) and solid-state time resolved spectroscopy experiments.

Finally, solvated [Co(*diox*)$_2$(4-CN-py)$_2$] crystals can undergo the VT interconversion reversibly without disruption of or damage to its crystallinity, which ensures the robustness of such materials and their potential to be used as sensors. Controlling and understanding the electronic properties of such bistable solid-state materials is a fundamental step towards the development of new devices.

ASSOCIATED CONTENT

The following files are available free of charge.

Experiment details, crystal and SCXRD data statistics (.pdf)

Crystallographic Information Files (CIF) 2058451-2058453 can be obtained from www.ccdc.cam.ac.uk/structures/. (.cif)

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Notes

The authors declare no competing financial interests.

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TOC SYNOPSIS

The photo-induced valence tautomerism of the ($\mathrm{Co}(\mathit{diox})_2(\text{4-CN-py})_2$) complex at 30K using hard X-rays and 450nm blue light with a very high yield of metastable states formation (80%) and the sequential de-excitation of such metastable states using 660nm red light.

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