Kent Academic Repository
Full text document (pdf)

Citation for published version

Francisco, Thiago M. and Gee, William J. and Shepherd, H.J. and Warren, Mark R. and Shultz, David A. and Raithby, Paul R. and Pinheiro, Carlos B. (2017) Hard X-ray-Induced Valence Tautomeric Interconversion in Cobalt-o-Dioxolene Complexes. The Journal of Physical Chemistry Letters, 8 (19). pp. 4774-4778. ISSN 1948-7185.

DOI

https://doi.org/10.1021/acs.jpclett.7b01794

Link to record in KAR

http://kar.kent.ac.uk/64721/

Document Version

Publisher pdf

Hard X-ray-Induced Valence Tautomeric Interconversion in Cobalt-*o*-Dioxolene Complexes

Thiago M. Francisco,[†] William J. Gee,[‡] Helena J. Shepherd,[‡] Mark R. Warren,[§] David A. Shultz,[‖] Paul R. Raithby,[⊥] and Carlos B. Pinheiro*,[†]

[†]Physics Department, Federal University of Minas Gerais, Belo Horizonte, 31270-901, Brazil
[‡]School of Physical Sciences, University of Kent, Canterbury CT2 7NZ, United Kingdom
[§]Diamond Light Source, Ltd., Harwell Science & Innovation Campus, Didcot OX11 0DE, United Kingdom
[‖]Department of Chemistry, North Carolina State University, Raleigh, North Carolina 27695, United States
[⊥]Department of Chemistry, University of Bath, Bath BA2 7AY, United Kingdom

Ⓢ *Supporting Information*

ABSTRACT: Valence tautomeric interconversion (VTI) is a reversible process occurring in metal complexes in which an intramolecular metal−ligand electron transfer is accompanied by a change of metal ion spin state, creating two switchable electronic states (redox isomers). Herein, we describe the low-temperature, 30−100 K, single-crystal study of the $[Co(diox)_2(4-CN-py)_2]$·benzene complex (**1**) (*diox* = 3,5-di-*t*-butylsemiquinonate ($SQ^{•-}$) and/or 3,5-di-*t*-butylcatecholate ($Cat^{2−}$) radical; 4-CN-py = 4-cyano-pyridine) using hard synchrotron X-ray radiation with different intensities. We demonstrate for the first time that hard X-rays can induce VTI, and that the interconversion molar fraction is dependent on both intensity and exposure time. This in turn shows that X-rays, as a probe, might be altering the very nature of many structures under investigation at low temperatures, and consequently their properties. Our findings add new perspectives to VTI studies and might be of significant interest to the entire community investigating photoresponsive complexes.
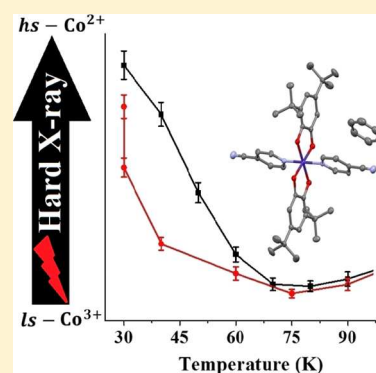
The development of solid-state "smart" materials that exhibit bistability, and can readily "switch" between two states when exposed to external stimuli such as changes in temperature, pressure or light irradiation, is one of the key challenges of modern materials chemistry. This is because such materials have potential for application as sensors, signal processors or in information storage devices.[1−3] Two of the most promising classes of material are spin-crossover[4−6] and valence tautomer complexes,[7−9] since both involve electronic transitions within a single metal center or within a molecular complex, without substantial disruption of the solid-state structure.

Complexes that undergo VTI present a reversible, entropy-driven rearrangement of intramolecular bonding electrons and a single-site spin crossover, that creates two switchable redox isomers with different spectroscopic and magnetic properties.[10] VTI can be induced in complexes of some metallic ions of type $3d^n$ ($4 \leq n \leq 7$) with a variety of different redox active ligands.[9] VTI has been reported to occur under physical stimuli such as change of temperature,[11] pressure,[12] and magnetic and electric fields.[13] VTI can also be modulated by chemical changes[14] and solvation.[15] Long-lived metastable states have also been observed as a result of light irradiation at very low temperatures in materials presenting VTI.[16,17]

A soft X-ray absorption spectroscopy (XAS) experiment on $[Co(Me_2tpa)(diox)][PF_6]$·toluene ($Me_2tpa$ = bis(6-methyl-(2-

pyridylmethyl)) (2-pyridylmethyl)amine) showed that soft X-rays (ca. 780 eV) themselves provide sufficient stimulus for the interconversion between two redox isomers as evidenced by the L_{III}-edge X-ray absorption spectrum, recorded at ca. 10 K, which shows the presence of both hs-$[Co^{2+}(SQ^{•-})_2]$ and ls-$[Co^{3+}(SQ^{•-})(Cat^{2−})]$ states.[18] It has also been shown that hard X-rays induce the formation of a trapped excited spin state in the spin crossover complex, $[Fe^{III}(bis(3-salicylidene aminopropyl)amine)py]BPh_4$ (py = pyridine).[19] This phenomenon has been described as hard-X-ray-induced excited-spin-state trapping (HAXIESST) by analogy to the common light-induced excited-spin-state trapping (LIESST) observed in many spin crossover complexes.[20] Co $K\beta$ X-ray emission and L-edge X-ray absorption spectroscopies were used to investigate the electronic configuration of valence tautomers at low temperature, suggesting the possibility of hard X-ray-induced VTI $[Co(diox)_2(Phe)]$ at 34 K (phe = phenantroline).[21] These results raise the question of whether hard X-rays could induce VTI, and what level of X-ray intensity would be required to stimulate such phenomenon. The answer to this question would not only be important for a whole plethora of complexes that exhibit photochromism, but it also concerns the

determination of the structure of metal complexes carried out by single-crystal X-ray diffraction using synchrotron radiation coupled with cryogenic crystal cooling. Therefore, it reveals whether X-rays, as a probe, might be altering the very nature of the structures under investigation, and consequently their properties.

Previously, we conducted a VTI study on single crystals of **1** over the temperature range of 90−300 K.[22] A noncooperative hs-$[Co^{2+}(SQ^{\bullet-})_2] \rightarrow ls$-$[Co^{3+}(SQ^{\bullet-})(Cat^{2-})]$ interconversion takes place during the cooling from 290 down to 90 K with pure hs-$[Co^{2+}(SQ^{\bullet-})_2]$ isomer being found above 290 K, while pure ls-$[Co^{3+}(SQ^{\bullet-})(Cat^{2-})]$ isomer is observed at around 100 K depending on the thermal history of the sample. Herein we report new results of a single crystal study of **1** at temperatures between 30 and 100 K, using synchrotron hard X-ray radiation (25516.4 eV) of different intensities.

The preparation of $[Co(diox)_2(4\text{-CN-py})_2]$ has been reported previously.[17] Benzene-solvated single crystal samples of **1** were grown by slow evaporation under an inert $N_{2(g)}$ atmosphere and stored in this condition until the beginning of the X-ray diffraction experiments. I19, the small molecule single crystal diffraction beamline at Diamond light source[23] was used to probe the effect of hard X-rays on the VTI in this complex in the temperature range between 30 and 100 K. Sample temperature was controlled during the experiments by a commercially available open-flow He cryostat (nHeliX, Oxford Cryosystems) apparatus with stability better than ±0.3 K.

Two experiments were undertaken in order to qualitatively assess the effects of the hard X-rays on the samples. In the first experiment (denoted HAX: hard X-ray), a single crystal of **1** was fast-cooled, in the dark, to 30 K and a data set was recorded using an X-ray beam without attenuation (about 10^{10} photons· s^{-1}, distributed over a spot of 0.1×0.1 mm^2). Subsequent data sets were recorded in the dark at 10 K intervals while heating the sample from 30 to 100 K. In a second experiment (denoted AHAX; 78% attenuated hard X-ray), data sets were recorded while a different sample was slowly cooled down from 290 to 30 K in the dark. The 78% beam intensity attenuation was achieved thanks to a 3 mm thick aluminum filter.[24] HAX and AHAX detailed experimental descriptions are given in the Supporting Information (SI).

The complex **1** crystallizes in the monoclinic space group $P2_1/c$, with two $[Co(diox)_2(4\text{-CN-py})_2]$ molecules in the unit cell ($Z = 2$), such that 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, the $diox$ ligands are superimposed, and so X-ray diffraction techniques are unable to distinguish the $SQ^{\bullet-}$ and/or Cat^{2-} forms in the ls-$[Co^{3+}(SQ^{\bullet-})$-$(Cat^{2-})]$ isomer.[21] The crystal data as well as representative refinement data are shown in Tables S5−S6 of the SI. Figure 1 shows the molecular structure and packing of **1**, at 30 K, as well as the atomic labeling scheme used for the selected atoms.

The new structure determinations at temperatures ranging between 30 and 100 K show that the overall geometry of **1** remains similar to that observed previously at 100 K.[21] Indeed **1** is geometrically ordered and shows the same packing and similar intermolecular interactions over the entire temperature range investigated. As shown in Figure 2, molecules of $[Co(diox)_2(4\text{-CN-py})_2]$ within the layer of interacting molecules (molecules in $b \times c$ plane) are linked by two major hydrogen bonds: C16−H···O2^i and C18−H···N2^{ii} ($i = x, y, 1 + z$; $ii = x, -y + 1/2, z - 1/2$).
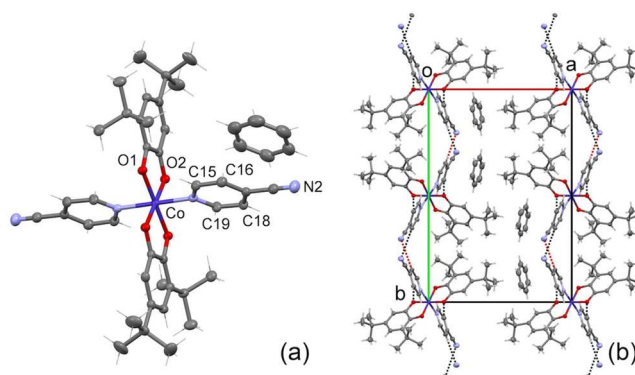

Figure 1. (a) The molecular geometry and (b) view of the crystal packing with some interactions of **1** at 30 K. Ellipsoids are drawn at the 50% of probability level. Hydrogen atoms are represented by sticks for the sake of clarity.
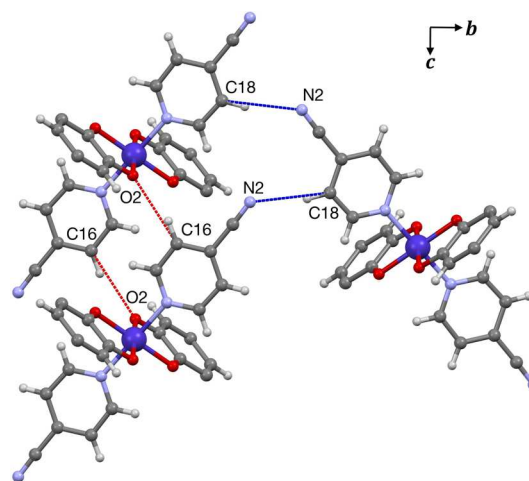

Figure 2. Intermolecular hydrogen bonds C_{ar}−H···O$_{diox}$ (red) and C_{ar}−H···N$_{cyano}$ (blue); C_{ar}, N_{cyano}, and O_{diox} are carbon atoms of the pyridine ring, nitrogen from the cyano group, and the oxygen atoms of the dioxolene group, respectively. t-Butyl groups were omitted for the sake of clarity.

Following the change of the electronic population of the metal orbitals observed in all cobalt dioxolene complexes during VTI,[9] three major reversible structural changes characterize the hs-$[Co^{2+}(SQ^{\bullet-})_2] \rightarrow ls$-$[Co^{3+}(SQ^{\bullet-})(Cat^{2-})]$ interconversion of **1**: (i) isotropic contraction of the Co−L (L = O1, O2, N1 atoms) coordination sphere, (ii) change of the relative orientation of benzene solvent molecules and cyanopyridine planes and (iii) shortening of the C15−H···O1 and C19−H···O1^i ($iii = -x, 1 - y, 1 - z$) intramolecular hydrogen bonds. C15, C16, C18, and C19 are atoms of the pyridine ring, N2 is the nitrogen atom of the cyano group, and O1 and O2 are the oxygen atoms of the dioxolene group binding the cobalt ion. Selected bond distances as well as the overlay of the structure of **1** at representative temperatures are shown in Tables S7−S8 and Figures S1 of the SI, respectively.

In general cobalt dioxolene complexes, Co^{2+}−L bond lengths are ca. 0.3 Å longer than similar Co^{3+}−L ones. Hence, the VTI can be characterized at each temperature by converting the refined Co−L distances in the Co first coordination shell obtained from single-crystal X-ray diffraction data into a molar fraction following the procedure proposed in Ribeiro et al.[22] This approach has no limitation other than the single crystal

sample quality that assures an accurate structural data refinement with high precise interatomic distances to compute the mole fraction. Figure 3 shows the calculated hs-$[Co^{2+}(SQ^{\bullet-})_2]$ molar percentage (mole fraction multiplied by 100) as a function of temperature for **1** for the HAX and the AHAX experiments described above.
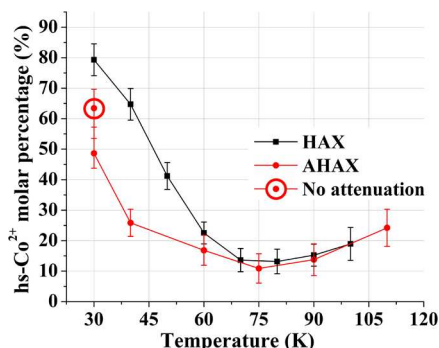

Figure 3. Metastable hs-$[Co^{2+}(SQ^{\bullet-})_2]$ isomer molar percentage during VTI under sample exposure to a nonattenuated X-ray beam (HAX) and to a 78% attenuated X-ray beam (AHAX). The encircled spot indicates the additional non attenuated data collection performed after AHAX experiment.

At low temperatures, where VTI free energy changes are largely determined by the enthalpy contributions, the valence tautomer ground state is characterized by unpopulated antibonding e_g^* orbitals, i.e., shorter metal−ligand bonds, and thus only the ls-$[Co^{3+}(SQ^{\bullet-})(Cat^{2-})]$ isomer of **1** was expected to be found in the absence of external stimulus like illumination.[16,17]

However, in the HAX experiment, irradiation of **1** induced the metastable hs-$[Co^{2+}(SQ^{\bullet-})_2]$ isomer appearance with maximum conversion observed at 30 K, with molar percentage of ca. 80%, with the remaining 20% being the ground state ls-$[Co^{3+}(SQ^{\bullet-})(Cat^{2-})]$ redox isomer. At temperatures above 30 K the molar percentage of the metastable hs-$[Co^{2+}(SQ^{\bullet-})_2]$ isomer reduces rapidly with only 15% being present at 70 K. Between 70−100 K it appears to be a slight increase in the percentage of the hs-$[Co^{2+}(SQ^{\bullet-})_2$ species, with a maximum of ca. 20% at 100 K.

The AHAX experiment performed using a different sample shows that lowering the temperature of **1** under an attenuated beam irradiation also resulted in the appearance of the metastable hs-$[Co^{2+}(SQ^{\bullet-})_2]$ redox state with a molar percentage reaching 50% down to 30 K. A final measurement performed at 30 K, using the same sample and collecting data with the same beam intensity used in the HAX experiment, results in hs-$[Co^{2+}(SQ^{\bullet-})_2]$ molar percentage increase to 65%. The 15% additional increase in molar fraction is due to the increase of the hard X-ray beam intensity. It is worth noting that the temperature profile of hs-$[Co^{2+}(SQ^{\bullet-})_2]$ molar percentage evolution below 70 K is quite different in both the HAX and AHAX experiments.

Figure 4 shows the dependence of the metastable hs-$[Co^{2+}(SQ^{\bullet-})_2]$ isomer molar percentage growth at ∼30 K as a function of the hard X-ray time exposure. The Co−L bond lengths used to compute the mole fraction were obtained from the structure refinements performed using partial data sets from the HAX and AHAX experiments (Tables S2 and S4 in the SI). In the HAX experiment, the first set is composed of four runs (first four points shown in its half exposure time); further and
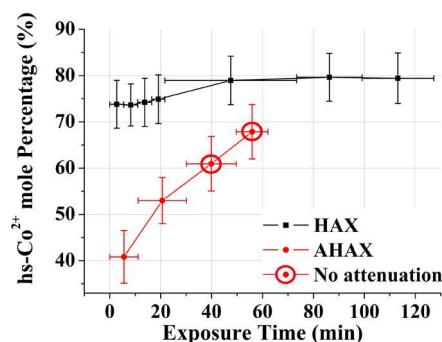

Figure 4. Exposure time dependence of the metastable hs-$[Co^{2+}(SQ^{\bullet-})^2]$ isomer molar percentage at ∼30 K in the different experiments. The horizontal bars indicate the duration of the partial X-ray diffraction data collection from which data was obtained.

without interruption, a second data set was collected, which is plotted as the last three points in the graph also shown in its half exposure time. In the AHAX experiment, the sample was irradiated with 78% of attenuation in the first two runs and then it was exposed to a nonattenuated hard X-ray beam. A modest increase of the metastable hs-$[Co^{2+}(SQ^{\bullet-})_2]$ isomer molar percentage in HAX as a function of X-ray exposure time and a significant increase in AHAX experiments both as a function of X-ray time exposure and as a function of the X-ray beam intensity can be observed. The horizontal bars in each point indicated the duration of each partial X-ray diffraction data collection from which data was obtained. The large vertical error bars observed reflect the low precision of the refined distances due to the low redundancy, low completeness and eventually lack of intense reflections of each used data set.

Notably, the irradiation of the samples with an intense hard X-ray beam in the HAX experiment seems to induce the metastable hs-$[Co^{2+}(SQ^{\bullet-})_2]$ isomer appearance with molar percentage of ca. 80% with no remarkable time dependence. The AHAX experiments, show a time dependence of the hs-$[Co^{2+}(SQ^{\bullet-})_2]$ metastable isomer mole fraction as evidenced by the molar percentage growth until ca. 40 min of X-ray exposure.

The appearance of the metastable hs-$[Co^{2+}(SQ^{\bullet-})_2]$ isomer in the HAX and AHAX experiments demonstrates that hard X-rays can trigger the VTI of **1** at low temperatures, an effect that we term hard-X-ray-induced valence tautomeric interconversion (HAXIVTI). Under the experimental conditions for this work, the hs-$[Co^{2+}(SQ^{\bullet-})_2]$ molar percentage grows to a maximum of ca. 80% at 30 K. A comparison of the HAX and AHAX experiments suggests a higher (80/50%) conversion to the metastable hs-$[Co^{2+}(SQ^{\bullet-})_2]$ isomer with increased X-ray intensity whereas a comparison of molar percentage evolution with time suggests a faster conversion to the metastable hs-$[Co^{2+}(SQ^{\bullet-})_2]$ with increased X-ray intensity. Hard X-ray irradiation induces reversible spin-crossover in iron complexes,[19] reversible VTI in **1**, and soft X-rays have been known to induce VTI in some complexes similar to **1**.[18] Therefore, the very nature of such phenomena are likely to be similar and triggered by the relaxation processes that follow electronic excitations caused by secondary electron generation after X-ray aborption.[18,19]

It is worth mentioning that the metastable hs-$[Co^{2+}(SQ^{\bullet-})_2]$ redox isomer photoexcitation of the complexes Co($diox$)$_2$L$_2$ [L = py, (4-OMe-py), (4-Me-py), (4-Me-py), (4-Br-py), (4-NO$_2$-py)] investigated using a SQUID magnetometer at 10 K,[11]

indicated a maximum conversion percentages approaching only ~30%. This behavior was attributed to the inability of the incident light to fully penetrate the opaque samples and promote VTI and/or to a photoinduced decay process as result of absorption of wavelengths of light by $hs\text{-}[Co^{2+}(SQ^{\bullet-})_2]$ form, thus future investigations to determine whether the final excitation process that leads to the hard X-ray VTI can also be modulated by light illumination are warranted.[18,25]

Hard X-rays have long been assumed to act as a noninteracting probe; however, our findings show the opposite effect. Hard X-rays might indeed substantially alter the structure related properties of the system under investigation and can, indeed, be used to populate VTI metastable states when optical excitation is limited by any sample characteristics or experimental setup.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

CIF files 1559584−1559598 contain the supplementary crystallographic data for this paper. They can be obtained free of charge from The Cambridge Crystallographic Data Centre (CCDC) via www.ccdc.cam.ac.uk/structures/. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpclett.7b01794.

X-ray experiment description, selected interatomic distances, and molecule superposition (PDF)

■ AUTHOR INFORMATION

Corresponding Author
*Address: Universidade Federal de Minas Gerais − Departamento de Física, Av. Antônio Carlos 6627 CEP 31270-901. Belo Horizonte, MG − Brazil. Tel +55-31-3409-6600. E-mail: cbpinheiro@ufmg.br.

ORCID
Thiago M. Francisco: 0000-0001-8722-4127
Helena J. Shepherd: 0000-0003-0832-4475
David A. Shultz: 0000-0001-8121-6812
Carlos B. Pinheiro: 0000-0002-8674-1779

Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

■ REFERENCES

(1) Sato, O.; Tao, J.; Zhang, Y.-Z. Control of Magnetic Properties through External Stimuli. *Angew. Chem., Int. Ed.* **2007**, *46* (13), 2152−2187.

(2) Sato, O. Dynamic Molecular Crystals with Switchable Physical Properties. *Nat. Chem.* **2016**, *8* (7), 644−656.

(3) Manrique-Juárez, M. D.; Rat, S.; Salmon, L.; Molnár, G.; Quintero, C. M.; Nicu, L.; Shepherd, H. J.; Bousseksou, A. Switchable Molecule-Based Materials for Micro- and Nanoscale Actuating Applications: Achievements and Prospects. *Coord. Chem. Rev.* **2016**, *308*, 395−408.

(4) Muñoz, M. C.; Real, J. A. Thermo-, Piezo-, Photo- and Chemo-Switchable Spin Crossover Iron(II)-Metallocyanate Based Coordination Polymers. *Coord. Chem. Rev.* **2011**, *255* (17−18), 2068−2093.

(5) Halcrow, M. A. Structure:Function Relationships in Molecular Spin-Crossover Complexes. *Chem. Soc. Rev.* **2011**, *40* (7), 4119.

(6) Gütlich, P.; Gaspar, A. B.; Garcia, Y. Spin State Switching in Iron Coordination Compounds. *Beilstein J. Org. Chem.* **2013**, *9*, 342−391.

(7) Pierpont, C. G. Studies on Charge Distribution and Valence Tautomerism in Transition Metal Complexes of Catecholate and Semiquinonate Ligands. *Coord. Chem. Rev.* **2001**, *216*, 99−125.

(8) Shultz, D. A. Valence Tautomerism in Dioxolene Complexes of Cobalt. *Magn. Mol. Mater. 5 Vol. Set* **2001**, 281−306.

(9) Tezgerevska, T.; Alley, K. G.; Boskovic, C. Valence Tautomerism in Metal Complexes: Stimulated and Reversible Intramolecular Electron Transfer between Metal Centers and Organic Ligands. *Coord. Chem. Rev.* **2014**, *268*, 23−40.

(10) Adams, D. M.; Hendrickson, D. N. Pulsed Laser Photolysis and Thermodynamics Studies of Intramolecular Electron Transfer in Valence Tautomeric Cobalt O-Quinone Complexes. *J. Am. Chem. Soc.* **1996**, *118* (46), 11515−11528.

(11) Schmidt, R. D.; Shultz, D. A.; Martin, J. D.; Boyle, P. D. Goldilocks Effect in Magnetic Bistability: Remote Substituent Modulation and Lattice Control of Photoinduced Valence Tautomerism and Light-Induced Thermal Hysteresis. *J. Am. Chem. Soc.* **2010**, *132* (17), 6261−6273.

(12) Roux, C.; Adams, D. M.; Itié, J. P.; Polian, A.; Hendrickson, D. N.; Verdaguer, M. Pressure-Induced Valence Tautomerism in Cobalt o-Quinone Complexes: An X-Ray Absorption Study of the Low-Spin [CoIII(3,5-DTBSQ)(3,5-DTBCat)(Phen)] to High-Spin [CoII(3,5-DTBSQ)2(Phen)] Interconversion. *Inorg. Chem.* **1996**, *35* (10), 2846−2852.

(13) Droghetti, A.; Sanvito, S. Electric Field Control of Valence Tautomeric Interconversion in Cobalt Dioxolene. *Phys. Rev. Lett.* **2011**, *107* (4), 047201.

(14) Bubnov, M. P.; Skorodumova, N. A.; Arapova, A. V.; Smirnova, N. N.; Samsonov, M. A.; Fukin, G. K.; Cherkasov, V. K.; Abakumov, G. A. Lattice-Modulated Phase Transition Coupled with Redox-Isomeric Interconversion of o-Semiquinone−Catecholato into Bis(o-Semiquinonato) Cobalt Complexes. *Inorg. Chem.* **2015**, *54* (16), 7767−7773.

(15) Mulyana, Y.; Poneti, G.; Moubaraki, B.; Murray, K. S.; Abrahams, B. F.; Sorace, L.; Boskovic, C. Solvation Effects on the Valence Tautomeric Transition of a Cobalt Complex in the Solid State. *Dalton Trans.* **2010**, *39* (20), 4757.

(16) Sato, O.; Cui, A.; Matsuda, R.; Tao, J.; Hayami, S. Photo-Induced Valence Tautomerism in Co Complexes. *Acc. Chem. Res.* **2007**, *40* (5), 361−369.

(17) Schmidt, R. D.; Shultz, D. A.; Martin, J. D. Magnetic Bistability in a Cobalt Bis(Dioxolene) Complex: Long-Lived Photoinduced Valence Tautomerism. *Inorg. Chem.* **2010**, *49* (7), 3162−3168.

(18) Poneti, G.; Mannini, M.; Sorace, L.; Sainctavit, P.; Arrio, M.-A.; Otero, E.; Criginski Cezar, J.; Dei, A. Soft-X-Ray-Induced Redox Isomerism in a Cobalt Dioxolene Complex. *Angew. Chem., Int. Ed.* **2010**, *49* (11), 1954−1957.

(19) Vankó, G.; Renz, F.; Molnár, G.; Neisius, T.; Kárpáti, S. Hard-X-Ray-Induced Excited-Spin-State Trapping. *Angew. Chem., Int. Ed.* **2007**, *46* (28), 5306−5309.

(20) Decurtins, S.; Gütlich, P.; Hasselbach, K. M.; Hauser, A.; Spiering, H. Light-Induced Excited-Spin-State Trapping in Iron(II) Spin-Crossover Systems. Optical Spectroscopic and Magnetic Susceptibility Study. *Inorg. Chem.* **1985**, *24* (14), 2174−2178.

(21) Liang, H. W.; Kroll, T.; Nordlund, D.; Weng, T.-C.; Sokaras, D.; Pierpont, C. G.; Gaffney, K. J. Charge and Spin-State Characterization of Cobalt Bis(o-Dioxolene) Valence Tautomers Using Co Kβ X-Ray Emission and L-Edge X-Ray Absorption Spectroscopies. *Inorg. Chem.* **2017**, *56* (2), 737−747.

(22) Ribeiro, M. A.; Stasiw, D. E.; Pattison, P.; Raithby, P. R.; Shultz, D. A.; Pinheiro, C. B. Toward Controlling the Solid State Valence Tautomeric Interconversion Character by Solvation. *Cryst. Growth Des.* **2016**, *16* (4), 2385−2393.

(23) Nowell, H.; Barnett, S. A.; Christensen, K. E.; Teat, S. J.; Allan, D. R. I19, the Small-Molecule Single-Crystal Diffraction Beamline at Diamond Light Source. *J. Synchrotron Radiat.* **2012**, *19* (3), 435−441.

(24) Hubbell, J. H.; Seltzer, S. M. Tables of X-ray Mass Attenuation Coefficients and Mass Energy-Absorption Coefficients (Version 1.4). [Online] available: http://Physics.Nist.Gov/Xaamdi [2017, August 15]; National Institute of Standards and Technology: Gaithersburg MD, 2004.

(25) Unruh, D.; Homenya, P.; Kumar, M.; Sindelar, R.; Garcia, Y.; Renz, F. Spin State Switching of Metal Complexes by Visible Light or Hard X-Rays. *Dalton Trans* **2016**, *45* (36), 14008−14018.