# Temperature-induced changes in the charge and spin density of valence tautomers probed by X-ray emission and Kβ-detected absorption spectroscopy

F. Otte[1,2], F.A. Lima[1], J. Rogalinski[1], J. Latarius[2], S. Jannuzzi[3], M. Riberio[4], C. Sternemann[2], C. Bressler[1]

[1]European XFEL Facility, FXE instrument, Schenefeld, Germany, [2]Technische Universität Dortmund, Fakultät Physik / DELTA, Dortmund, Germany, [3]MPI for Chemical Energy Conversion, Mülheim, Germany, [4]Universidade Federal do Espirito Santo, Vitória, Brazil, **florian.otte@xfel.eu**

Valence tautomeric transitions (VT) are characterized by stimulated intramolecular charge transfer and single-site spin crossover [1,2]. Similar to spin-crossover and charge transfer induced spin transitions, valence tautomers have been studied extensively as candidates for electronically-labile molecular systems, which can be essentially "flipped" between two electronic states by relatively small changes in temperature, pressure or by laser excitation [1-8]. Cobalt-based organometallic compounds with redox-active *o*-dioxolene ligands are of special importance in this field, as their metal- and ligand frontier orbitals tend to be of similar energy, thus fulfilling an important prerequisite for VT to occur [1,2]. The nature of the charge transfer and the metal-ligand magnetic exchange interaction is still an open question and has been addressed by density functional theory (DFT) calculations, and speculated based on Co Kβ X-ray Emission Spectroscopy (XES) measurements [8,9].

Here we present a series of temperature-dependent Kβ and valence-to-core (VtC) XES data as a means to further elucidate the nature of the magnetic exchange interaction and ancillary ligand contribution in cobalt valence tautomers from the o-dioxolene family. Exploratory Co Kβ resonant XES are also being explored and will provide further insight into the mechanisms of VT transitions in those systems.

F. Otte acknowledges funding via BMBF (05K16PE1). We thank the beamline staff of CLAESS, ALBA, Spain and BL9, DELTA, Germany for help and providing synchrotron radiation for this project.

**References**

[1] - D.A. Shultz, in Magnetism: Molecules to Materials II 281-306 (Wiley-VCH Verlag GmbH & Co. KGaA, 2003).
[2] - D.N. Hendrickson & C.G. Pierpont, in 1, 63-95 (2004).
[3] - C. Boskovic, in *Spin-Crossover Materials* 203-224 (John Wiley & Sons Ltd, 2013).
[4] - O. Sato, A. Cui, R. Matsuda, J. Tao & S. Hayami, *Acc. Chem. Res.* 40, 361-369 (2007).
[5] - O. Sato, J. Tao & Y.-Z. Zhang, Angew. Chem. Int. Ed. Engl. 46, 2152-87 (2007).
[6] - A. Dei, D. Gatteschi, C. Sangregorio & L. Sorace, doi:10.1021/AR0200706 (2004).
[7] - E. Evangelio & D. Ruiz-Molina, Comptes Rendus Chim. 11, 1137-1154 (2008).
[8] - R.D. Schmidt, D.A. Shultz & J.D. Martin, Inorg. Chem. 49, 3162-3168 (2010).
[9] - H.W. Liang et al., Inorg. Chem. 56, 737-747 (2017).