

## Hard X-ray-Induced Valence Tautomeric Interconversion in a Cobalt Complex

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[Co(*o*-diox)<sub>2</sub>(4-CN-py)<sub>2</sub>]-benzene (*o*-diox = 3,5-di-*t*-butylsemiquinonate (*SQ*<sup>•−</sup>) and/or 3,5-di-*t*-butyl-catecholate (*Cat*<sup>2−</sup>) radical; 4-CN-py = 4-cyano-pyridine) (**1**) (figure 1) is a valence tautomer [1] showing a charge transfer between the redox-active ligand and the cobalt accompanied by a change of metal ion spin state [2]. Such processes are reversible and create two switchable electronic states *hs*-[Co<sup>2+</sup>(*SQ*<sup>•−</sup>)<sub>2</sub>] and *ls*-[Co<sup>3+</sup>(*SQ*<sup>•−</sup>)(*Cat*<sup>2−</sup>)] that can be interconverted by external stimuli such as temperature and illumination [3]. In **1** pure *hs*-[Co<sup>2+</sup>(*SQ*<sup>•−</sup>)<sub>2</sub>] state is found above 290 K whereas almost pure *ls*-[Co<sup>3+</sup>(*SQ*<sup>•−</sup>)(*Cat*<sup>2−</sup>)] state is observed below 100 K depending on the thermal history of the sample. The structure of **1** was further investigated by single crystal X-ray diffraction at the IL9 Beamline of the Diamond synchrotron radiation facility [4] using hard X-ray radiation (0.48590 Å) in temperatures ranging from 300 K down to 30 K. Initially a sample was fast cooled to 30 K and successively exposed to an X-ray beam without attenuation from 30 to 100 K (HAX) in the darkness. A second sample was fast cooled to 30 K and then illuminated with an intense LED white light for 60s. After illumination, a new series of single crystal X-ray diffraction experiments was performed from 30 K up to 100 K (HAXWL) in the darkness, using an attenuated X-ray beam when compared with the first experiment run. A third sample was measured in the darkness, during slow cooling from 300 down to 30 K with an attenuated X-ray beam (Attenuated HAX). Surprisingly, **1** was found to present hard X-ray responsive behaviour yielding a metastable *hs*-[Co<sup>2+</sup>(*SQ*<sup>•−</sup>)<sub>2</sub>] redox isomer at temperatures near 30 K with ~80% mole percentage conversion (Figure 2). Hard X-rays have long been assumed to act as a non-interacting probe, however our findings show the opposite effect: **1** display reversible valence tautomer interconversion induced by hard X-ray irradiation. Thus, hard X-rays might alter the structure related properties of valence tautomers and can, indeed, be used to populate metastable states when optical excitation is limited by any sample characteristics or experimental setup.

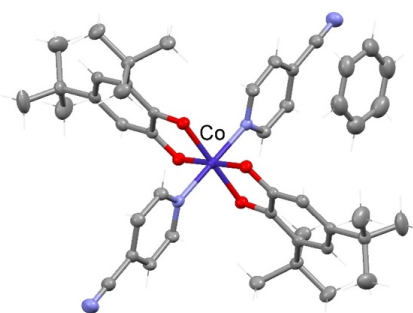


Figure 1: [Co(*o*-diox)<sub>2</sub>(4-CN-py)<sub>2</sub>]-benzene structure.

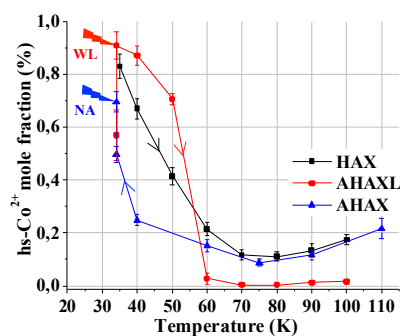


Figure 2: metastable *hs*-[Co<sup>2+</sup>(*SQ*<sup>•−</sup>)<sub>2</sub>] redox isomer appearance in [Co(*o*-diox)<sub>2</sub>(4-CN-py)<sub>2</sub>]-benzene.

WL=White Light, NA, non attenuated.

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