

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

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[Co(*o*-diox)₂(4-CN-py)₂]·benzene (*o*-diox = 3,5-di-*t*-butylsemiquinonate (SQ^{•-}) and/or 3,5-di-*t*-butylcatecholate (Cat²⁻) 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*-[Co²⁺(SQ^{•-})₂] and *ls*-[Co³⁺(SQ^{•-})(Cat²⁻)] that can be interconverted by external stimuli such as temperature and illumination [3]. In **1** pure *hs*-[Co²⁺(SQ^{•-})₂] state is found above 290 K whereas almost pure *ls*-[Co³⁺(SQ^{•-})(Cat²⁻)] 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 techniques using hard X-ray radiation (0.48590 Å) in temperatures ranging from 300 K down to 30 K. A single crystal suitable for X-ray diffraction experiments was mounted in a capton loop and transferred to the X-ray diffraction goniometer of the IL9 Beamline of the Diamond synchrotron radiation facility [4]. Initially the 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. Afterwards, the same sample was fast cooled to 30 K a second time 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. The sample was then heated to 300 K and 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 behavior yielding a metastable *hs*-[Co²⁺(SQ^{•-})₂] redox isomer at temperatures near 30 K with *ca.* 80% mole fraction conversion. Fast cooling of the samples from 100 K to 30 K followed by illumination with white light and attenuated hard X-rays beam radiation exposition also induced *ca.* 80% mole fraction conversion (Figure 2). **1** is the first valence tautomer displaying metastable mole fraction interconversion at low temperature investigated by single crystal X-ray diffraction techniques.

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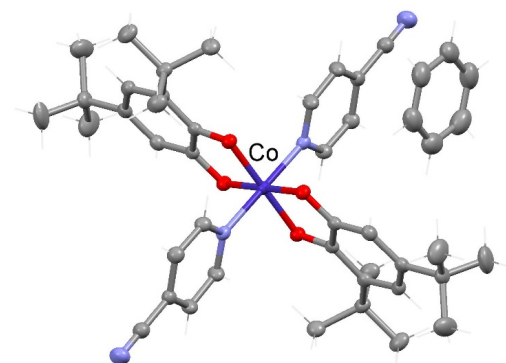


Figure 1: [Co(*o*-diox)₂(4-CN-py)₂]·benzene structure.

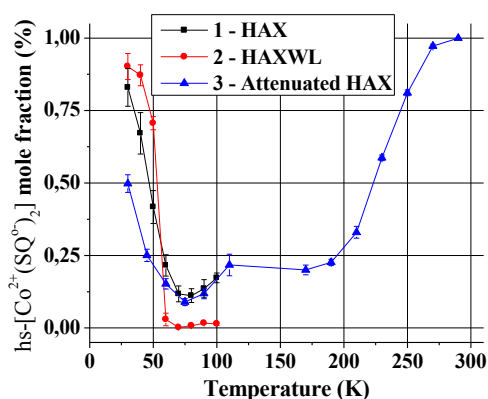


Figure 2: *hs*-Co²⁺ mole fraction change during cooling (3) and during the metastable *hs*-[Co²⁺(SQ^{•-})₂] redox isomer appearance (1,2).

Keywords: Photo-induced valence tautomerism, dioxolene cobalt complex, X-ray diffraction.