

Temperature and time-resolved XANES studies of novel valence tautomeric cobalt complex

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Valence tautomers are characterized by different electron density distributions, where metal-to-ligand electron transfer accomplishes interconversion between tautomers [1]. These compounds are unique model systems that can help study electron transfer mechanisms and find applications as sensors and displays or storage and fast optical switching devices. Wherein the valence tautomeric interconversion can be thermally, magnetically or radiatively driven. Among transition metal complexes cobalt complexes with redox-active ligands have been shown to undergo a valence tautomeric interconversion between high-spin and low-spin forms [2, 3].

This study is devoted to optical and x-ray structure characterization of novel (N-cyclohexyl-2-iminopyridine)(3,6-di-*tert*-butyl-*o*-benzosemiquinonato)(3,6-di-*tert*-butyl-catecholato) (Co²⁺) cobalt complex. We have monitored the transition induced both by temperature and laser stimuli. Complexes were dissolved in toluene. X-ray pump-probe study was performed at the Super-XAS beamline of the Swiss Light Source, Villigen, PSI. A green nanosecond laser with 532 nm wavelength was operated at 150 kHz repetition mode. We accumulated an X-ray fluorescence signal for different delays after laser excitation pulse with 20 ns time resolution for each energy point. Then principal component analysis was applied for the whole data set.

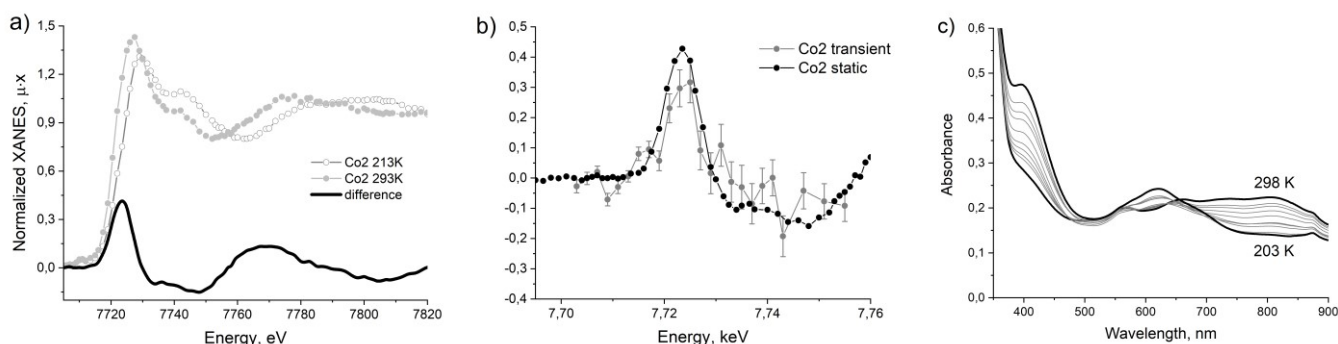


Figure 1. (a) Co K-edge XANES measured for Co²⁺ sample at 213K and 293K in a solution, (b) transient difference signal after laser excitation for Co²⁺ and (c) temperature dependence of UV-Vis spectrum for the Co²⁺ sample in toluene.

Fig. 1 shows XANES and optical results for one of the studied cobalt complexes. According to XANES, change in the cobalt oxidation and spin state can be observed when temperature decreases below 240 K (Fig.1(a)). The time-resolved transient difference shown in figure 1b can be compared to the static difference obtained at low and high temperatures (Fig.1b). Kinetics of the transient signal decay for 213 K can be approximated by a monotonic exponential decay with a characteristic time of 250±50 ns. Low-temperature UV-Vis spectra show intensity decreasing of a broad band at 800 nm and increase bands at 600 nm and 395 nm (Fig.1(c)). The band at 700 – 850 nm shows the high spin Co^{II} tautomer transition and has likely a metal-to-ligand charge transfer nature. The peak at ~600 nm characterised the low spin Co^{III} tautomer and caused by the ligand-to-metal charge transfer. The appearance of isosbestic points during cooling is strong evidence that only two different species are present in the solution [2]. Obtained results confirm the presence of a valence tautomeric transition in the cobalt complex under study. Our measurements indicate that Co^{II} is transformed into Co^{III} under temperature decrease while reverse transition can be induced both under the influence of temperatures and laser radiation.

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