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

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VT transition from the high-spin Co^{II} to low-spin Co^{III} state was observed for complex (N-cyclo-hexyl-2-iminopyridine)(3,6-di-*tert*-butyl-*o*-benzosemiquinonato)(3,6-di-*tert*-butyl-catecholato)cobalt in both solid and liquid form. For the first time we demonstrate the low-temperature nanosecond pump-probe XANES experiment revealing the valence tautomeric transition in a solution of Co complex. Reversible transition was induced both under the temperature and laser radiation stimuli.

Keywords: valence tautomerism; Co complex; pump-probe XANES;

Nowadays, special attention is paid to the development of future data recording, storage and switching molecular devices.^{1,2,3} For these needs, valence tautomeric (VT) metal complexes are actively developed and investigated.⁴ VT compounds undergo conversion-between tautomers due to a reversible intramolecular electron transfer between redox-active ligands and a redox-active metal. Such transitions lead to significant and reversible changes in the structural, optical, and magnetic properties of the metal complexes. Thereby, VT complexes are potential candidates for magneto-optical sensors, switches and molecule-based memory units.^{5,6} Among various VT compounds^{7,8,9} Co complexes with various redox-active quinone ligands have been extensively studied^{10,11,12}.

Decades ago D.M. Adams and D.N. Hendrickson have recorded electronic absorption spectra at variable temperatures in toluene of four cobalt bis-*o*-quinonato complexes of general composition [Co(3,5-DTBSQ)₂(N[^]N)] (where 3,5-DTBSQ⁻ charged forms of 3,5-di-*tert*-butyl-*o*-quinone and diiminium ligand N[^]N = 1,10-phenanthroline, 2,2'-dipyridine, 4,4'-dimethyl-dipyridine and 4,4'-diphenyl-dipyridine) to elucidate the factors controlling the VT interconversion process.¹³ The temperature dependence of the electronic absorption spectra showed dramatic changes with the appearance of isosbestic points during heating and cooling processes. The authors carried out a theoretical analysis of temperature depending VT process in solution using quantum mechanical theory of radiationless transitions. They concluded that the VT transformation is

driven by entropy and back transition involves quantum mechanical tunnelling.

As X-ray absorption near-edge structure (XANES) and X-ray emission spectroscopy (XES) are sensitive to the charge state of 3d metal and structural rearrangements of organic ligands, they are well-suited methods for VT metal complexes investigation. In the work¹⁴ authors combined K_β XES with Co L-edge XAS to investigate VT states of Co(phen)-(3,5-DBQ)₂ and Co(tmeda)(3,5-DBQ)₂ complexes. They demonstrated that the low-temperature valence tautomer could be described as a low spin Co^{III} and the high-temperature valence tautomer as a high spin Co^{II}. Herewith, Co K_β XES spectra at 375 K for both complexes showed similar HS Co^{II} electronic configuration. Moreover, the authors observed the occurrence of soft X-ray-induced VT in low-temperature L-edge XAS.

Time-resolved pump-probe XANES is a relatively new and challenging method, which can unravel the nature of short-lived excited states.^{15,16,17} Employing it to the transition metal complexes such as VT materials gives valuable information on excited molecular states and electron transfer processes.^{18,19,20} In recent work²¹ Ryan Ash et al. demonstrated application of M_{2,3}-edge XANES spectroscopy with 40 fs time resolution to study the mechanism and time scale of ultrafast VT in crystalline Co^{III}(Cat-N-SQ)(Cat-N-BQ) complex. Their result showed that ultrafast core-level M-edge XANES allows separation of vibrational and electronic relaxation transition from hot HS Co^{II} state to the LS Co^{III} ground state. However, there is still just a few works that provided transient XANES data for Co systems with VT.

Moreover, to the best of our knowledge, a pump-probe XANES experiment with VT complexes dissolved in liquid has not yet been demonstrated. Both liquid and solid state experiments are essential since the effects of intermolecular interactions affect the parameters of the VT transition, such as temperature, hysteresis and intermediate phases.²² In our work, we present the technical feasibility of such an experiment for the Co complex with (N-cyclo-hexyl-2-iminopyridine)(3,6-di-*tert*-butyl-*o*-benzosemiquinonato)(3,6-di-*tert*-butyl-catecholato) ligand.

Laser pump – X-ray probe study was performed at the Super-XAS beamline of the Swiss Light Source, Villigen, PSI. We used the Si(111) monochromator and asynchronous X-ray photon counting regime,²³ which provided 20 ns time resolution. A tungsten foil with a 50 μm pinhole was placed on the nozzle to allow laser/X-ray alignment. We placed Avalanche photodiode (APD) fluorescent - detector with a Z-1 filter and Soller slits close to the jet. A green nanosecond laser (DS20HE-532 from Photonics Industries) with 532 nm wavelength was operated at a 150 kHz repetition rate. Full laser power before the sample chamber was measured as 6 W. Laser pulse width was 20 ns. Co K-edge spectra were initially measured in a static mode before and after cooling to confirm the VT transition. The X-ray photon counting scheme was changed then to time-tagged photon counting, and pump-probe spectra were registered in the asynchronous mode under pulsed laser illumination at the lowest temperature

Figure 1. Scheme of experimental pump-probe XAS setup at the Super-XAS beamline, Swiss Light Source.

The scheme of the experiment is presented in Figure 1. The cooling system consisted of two Dewar vessels filled with ethanol and dry ice. The first Dewar contained a vessel with the sample solution in toluene (the total volume of the sample circulating in the system was about 80 ml). The second Dewar contained a coil pipe with the circulating sample. The opened part (nozzle) of the jet was inside the gas-tight chamber.

Figure 2. Structure of complex Co2.

Complex **Co2** (Figure 2) was synthesized by exchange reaction of tris-*o*-semiquinonato cobalt complex with corresponding iminopyridine (Figure S1).

We carried on a low-temperature UV-Vis spectroscopic study of **Co2** complex dissolved in toluene in transmittance mode using a custom assembled cell. Gradual changes in optical properties were occurring upon decreasing temperature (Figure 3). The optical absorption spectra indicated a VT transition similar to that demonstrated in.^{13,24}

Figure 3. Temperature resolved UV-Vis spectra of the **Co2** toluene solution.

At lower temperatures, the intensity of a broad band at 800 nm decreases, while bands at near 600 nm and 395 nm increase. The band at 700 – 850 nm is characteristic of the HS Co^{II} tautomer and has likely a metal-to-ligand charge transfer nature.^{13,24} At 203 K the peak at ~620 nm characterises the LS Co^{III} tautomer. It originates from the ligand-to-metal charge transfer.²⁵ The band at 395 nm increases along with sample cooling and includes the π - π^* ligand-based transition in the LS Co^{III} tautomer.^{26,27} The appearance of isosbestic points at near 560 nm and 657 nm during cooling is strong evidence that only two different states were present in the solution.¹³

VT transition in solution is observed at lower temperatures compared to solid state (see Figure 4 below). The magnetic moment of **Co2** in crystal slowly increases from 1.7 μ_B at 50 K to 2.1 μ_B at 260 K (Figure 4a). It decreases to 0.75 μ_B upon cooling to 2.0 K due to intermolecular antiferromagnetic interactions. The beginning of VT transformation is observed as fast increase of the magnetic momentum above 260 K.

FTIR spectra in the Figure 4b further confirm the VT transition in the crystalline phase above room temperature. In contrast to the UV-vis data measured in solution, no evident changes occur in FTIR spectra upon cooling. In agreement with magnetic moment measurements, the crystalline sample at room temperature is characterized as the LS Co^{III} state. Spectra recorded during heating above

Figure 4. (a) Magnetic moment (in solid) and (b) temperature-resolved FTIR spectra for the powder in the range 193 K - 373 K.

the VT transition. The modelling was performed within density functional theory (DFT) in Gaussian 16.²⁹ Three functionals were compared, namely PBE0,³⁰ B3LYP*³¹⁻³³ and TPSSH^{34,35} using Def2-TZVP basis set.³⁶ The calculated spin density distribution (q_s^{Co}) is presented in Table S1. High-spin structures contain three unpaired electrons on the cobalt ion, which indicates the HS Co^{II} state of the metal. For the low-spin state of the molecule, this parameter does not exceed 0.1, thus confirming the LS Co^{III} state of the metal. The relative energies of the isomers calculated with the PBE0 and B3LYP* functionals show the energetic preference of the high-spin state (HS Co^{II}), which is inconsistent with the existence of VT in the complex. Correct results were obtained with the TPSSH functional only. The values of the operator $\langle S^2 \rangle$ given in the Table S1 deviate slightly from those expected for the corresponding spin states (8.75 and 0.75), which indicates slight spin contamination (mixing of spin states) in the obtained structures.

In contrast to the controversial values of the HS-LS energy differences the DFT calculations predict similar values of the bond lengths between the metal-donor atoms for all three functionals (Table S2). The variation of these distances between the two spin states is in agreement with the expected VT transition. Smaller Co-O,N bond lengths in the LS Co^{III} state are observed for all applied functionals. For all geometries the bond length Co-N is always longer than Co-O. Both observations are the consequence of Coulomb interactions of Co³⁺ - Cat²⁻ versus Co²⁺ - SQ⁻ where slightly negatively charged iminopyridine affects the Co-N bonds lengths.

We measured cobalt K-edge XANES during cooling of the sample dissolved in toluene. In agreement with UV-vis measurements, the cobalt oxidation and spin state change below 240 K (Figure 5a). The shift of all spectral features to the higher energies upon cooling indicates valence state transition accompanied by strong structural changes in the complex.³⁷ According to the semi-empirical Natoli's rule, this shift indicates that the transformation from HS Co^{II} to LS Co^{III} induces the shortening of Co-O and Co-N bonds, in agreement with the DFT calculations and EXAFS analysis (Table S3).

The Co K-edge XANES spectra were calculated for the optimized structures using finite difference approach and compared to the experimental data (Figure S2). All theoretical spectra independently on the chosen functional show a good agreement with experimental data. The most significant deviation was observed for the LS Co^{III} geometry obtained within B3LYP* approximation. As the best result we have chosen the spectra calculated for TPSSH functional (Figure 5a) since only this potential provides correct energy values.

The next question that we have addressed was about the Co charge and spin state in the LS Co^{III} complex after photoexcitation. Pump-probe XAS has a high sensitivity and possibility to probe short-lived states with a lifetime in different time domains. Since the initial LS Co^{III} state is accumulated at low temperature, we have modified the setup to enable experiments for liquid samples at low temperature.

Excitation has been performed at 532 nm, which is the high energy side of the LMCT band. Data obtained using the pump-probe method are shown in Figure 5b.

Figure 5. (a) Co K-edge XANES spectra measured for **Co2** sample at 213K and 293K in a toluene solution and calculated for DFT-optimized structures within TPSSH functional (b) averaged transient difference XANES signal after laser excitation for **Co2**. The shape of the transient did not vary in the studied time delay range. Inset: kinetics of the amplitude of difference signal.

Principal component analysis of the spectra series measured with 20 ns step has indicated that only two components were present: initial LS Co^{III} state and the photo-induced state. From the comparison of the pump-probe transient spectrum with the difference between HS Co^{II} and LS Co^{III} states obtained by changing the temperature, we can conclude that HS state was formed due to photoexcitation. Within our time resolution, we do not see any signatures of LMCT state before spin transition (LS Co^{II}), which should have a significantly different local structure compared to HS Co^{II} and therefore easily distinguishable XAS spectrum. The lifetime of photo-induced HS Co^{II} state estimated through exponential fitting as 250 ± 50 ns (Figure 5b inset, red line is a

monoexponential decay fit) agrees with values reported for related compounds obtained using the optical pump-probe method.¹³

In conclusion, we observed valence tautomeric transition for **Co2** complex with N-cyclohexyl-2-iminopyridine and 3,6-di-*tert*-butyl-*o*-benzosemiquinonato ligands upon temperature variation both in a liquid form and a powder. In agreement with magnetic moment measurements, FTIR spectra demonstrated noticeable changes only above 363 K. The solid sample at room temperature was characterized as the LS Co^{III} state while the optical absorption spectra and Co K-edge XANES spectra in the toluene solution confirmed the HS Co^{II} state. At 213 K we registered a transient laser pump – X-ray probe signal in the **Co2** toluene solution that reproduced the difference between temperature stabilized HS and LS states. The relaxation kinetics to the ground state occurred with a time constant of 250 ± 50 ns. Our results indicate that reversible transition in the studied complex could be induced both under the influence of temperature and laser radiation. This experiment opens new perspectives for the pump-probe experiments for liquid samples at low temperatures.

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Supporting Information is available on http://dx.doi.org/10.1246/cl.*****.

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