

Photoinduced Processes in Cobalt-Complexes: Condensed Phase and Gas Phase

F. Rupp¹, K. Chevalier¹, M. M. N. Wolf¹, H. -J. Krüger², C. v. Wüllen², Y. Nosenko², G. Niedner-Schattburg², C. Riehn² and R. Diller¹

¹Dept of Physics, Univ. Kaiserslautern, 67663 Kaiserslautern, Germany

²Dept. of Chemistry, Univ. Kaiserslautern, 67663 Kaiserslautern, Germany

Abstract. Femtosecond time-resolved, steady-state spectroscopic methods and quantum chemical calculations are employed to study ultrafast photoinduced processes in [Co(III)-(L-N₄Me₂)(dbc)](BPh₄) and [Co(II)-(L-N₄tBu₂)(dbsq)](B(p-C₆H₄Cl)₄) and to characterise the transient redox- and spin-states in condensed and gas phase.

1 Introduction

Metal complexes undergoing valence tautomerism (VT) and spin-crossover (SCO) by external stimuli may be utilized as novel molecular switches[1]. Here we study ultrafast photoinduced processes in the first cobalt(II) semiquinonate complex [Co(II)-(L-N₄tBu₂)(dbsq)](B(p-C₆H₄Cl)₄) (**Cpd2**) that displays SCO properties rather than VT, and for comparison in a related cobalt(III) catecholate [Co(III)-(L-N₄Me₂)(dbc)](BPh₄) (**Cpd1**)[2], in both condensed and gas phase (dbsq: di-*tert*-butylsemiquinonate (Sq), dbc: di-*tert*-butylcatecholate (Cat)). In combination with quantum chemical calculations this approach allows to follow and characterize transient valence states and molecular structure, spin states[3,4], magnetization[5], energy flow, fragmentation patterns as well as the impact of solute/(micro-) solvent interaction.

2 Condensed phase: Femtosecond time-resolved pump-probe-spectroscopy

After photoexcitation of **Cpd2** dissolved in acetonitrile-d₃ at 1075 nm we probe in the visible/near-infrared (data not shown) and mid-IR range (Figure 1 (top)) for dynamical and structural information on the transient species[3]. A bi-exponential fit of the transient absorption yields two time constants $\tau_1 \approx 1$ ps and $\tau_2 \approx 9$ ps. During the photocycle an electron of the Co(II) atom of **Cpd2** is suggested to be transferred to the Sq coligand due to a metal-to-ligand-charge-transfer (MLCT) that leads to the formation of the Co(III)-Cat species with life times τ_1 and τ_2 , respectively, but different spin multiplicity. The negative net signals in the transient difference spectra in Figure 1 (top) clearly match the peak positions in the ATR-spectrum of **Cpd2** (solid) in Figure 1 (middle) and show the bleach of the ground state in the mid-IR at several band positions, e.g. 1176 cm⁻¹. The calculated stick spectrum (B3LYP, disp.-corr., TZVP basis, scaled 0.98) in Figure 1 (middle) clearly reproduces the experimental ATR-spectrum. The strong positive net signal around 1450 cm⁻¹ indicates the formation of the intermediate Cat species, taking into account that the absorption of the

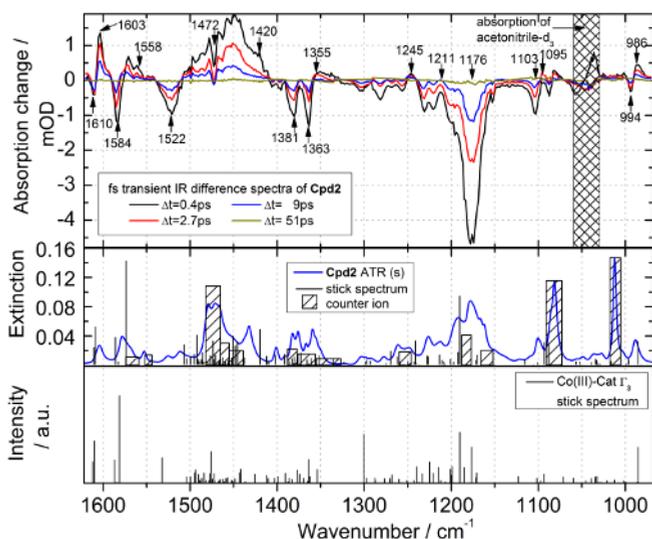


Fig. 1. Top: Transient mid-IR absorbance difference spectra of **Cpd2**/acetonitrile- d_3 at selected delay times between 0.4 ps (strong signal) and 51 ps (weak signal) after photo-excitation at 1075 nm and room temperature. Middle: For comparison steady state ATR-spectrum (solid) of **Cpd2** with calculated stick spectrum. Bottom: Calculated spectrum of Co(III)-Cat. Solvent and counter ion contributions shaded.

diamagnetic **Cpd1** is significantly higher around 1450 cm^{-1} (data not shown). On grounds of the femtosecond time-resolved and steady state measurements, as well as the quantum chemical calculations, the following reaction scheme is suggested: After the photoexcitation of **Cpd2** the system relaxes with less than 200 fs (time-resolution) into two Cat states, Γ_2 and Γ_3 . Γ_3 is supposed to be a diamagnetic Co(III)-Cat with $S=0$ and life time $\tau_2 \approx 9\text{ ps}$ (cf. Figure 1 (bottom)) and Γ_2 to be a Co(III)-Cat, but with $S=1$ and life time $\tau_1 \approx 1\text{ ps}$. The ground state of **Cpd2** is a ferromagnetically coupled triplet state with $S=1$. Therefore the spin-forbidden transition from singlet $S=0$ to triplet $S=1$ with τ_2 is roughly one order of magnitude slower than the allowed singlet-singlet transition with lifetime τ_1 . This tentative model will be advanced by further time-resolved as well as steady-state studies and quantum chemical calculations on similar complexes in order to identify vibrational marker bands for the assignment of the various redox- and spin-states.

3 Gas phase: Collision-induced dissociation and photofragmentation studies

In preparation of gas phase femtosecond time-resolved pump-probe spectroscopy employing photo-induced fragmentation, the ground state fragmentation patterns are investigated. The combination of electrospray ionization mass spectrometry (ESI-MS) with laser photofragmentation allows for a structural and dynamical investigation of isolated gas phase species. The ionic species are produced by the electrospray process from a liquid solution (acetonitrile) and subsequently stored and mass selected with isotopic resolution in a 3D ion trap (Bruker amaZon series). **Cpd1** and **Cpd2** gave relatively clean mass spectra in the cation mode with singly (and doubly charged) species at m/z 547.3 (273.5) and m/z 631.3 (315.5), respectively. The collision-induced dissociation (CID) of these cations resulted in the neutral loss of a Cat or Sq group (identical m/z 220) and in parallel the loss of a methyl (m/z 15) and tert-butyl group (m/z 57) as fragmentation channels (Figure 2 (left, top)). The dioxolene loss is the major channel for the Sq, whereas for the Cat the methyl loss dominates. We recorded also CID fragment yield curves in order to elucidate the binding energies (activation energies for dissociation) of the Sq vs. the Cat unit. Clearly, the activation energy for dissociation for the cation of **Cpd2** is larger than that for the cation of **Cpd1** (Figure 2, (bottom)). Hence, we conclude the Sq being the more stable species. From the interrogation of the stored species with a ns-

IR laser we have obtained infrared multiple photon dissociation (IRMPD) spectra of the two different Co-complexes in the C-H stretching region (Figure 2 (right)).

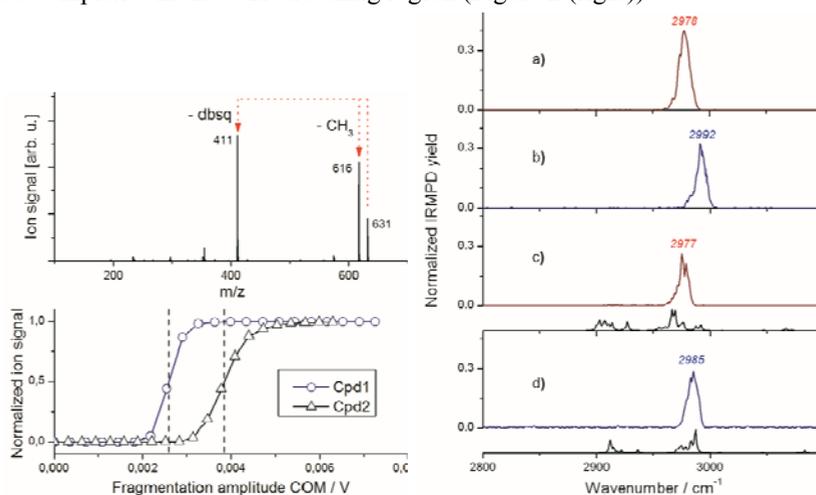


Fig. 2. Left: Top: Electrospray ionization mass spectrum of **Cpd2** with indication of fragmentation channels. Bottom: Fragment yield curves for collision-induced dissociation of the cations of **Cpd2** and **Cpd1**. Fragmentation voltage converted to center-of-mass (COM) values. **Right:** IRMPD spectra of the electrospray ionized a), c) singly and b), d) doubly charged cations of a)-b) (**Cpd1**) and c)-d) (**Cpd2**) complexes. Black/lower trace in c) and d): spectra obtained by the DFT/B3LYP/cc-pVTZ, scaled by 0.96.

The fragmentation channels resulting from collision or IR induced dissociation are the same. The spectra (normalized total fragment yield as a function of laser frequency) are very sparse and only one band was observed. The ground states of the Sq and the Cat are not distinguishable from this band. A clear blue shift by 10-20 cm⁻¹ upon increase of the charge state was detected. DFT calculations reproduce the band structure and blue shift reasonably well. These IR fragmentation studies, in particular the determination of the ground state fragmentation channels, branching ratios and product yields for Sq vs. Cat complexes are a prerequisite for femtosecond pump-probe studies under the same mass-spectrometric conditions for electronic excited states. The goal being to compare electronic dynamics of SCO and VT compounds under different solvation conditions (gas phase vs. solution).

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