Valence Tautomerism

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Soft-X-ray-Induced Redox Isomerism in a Cobalt Dioxolene Complex**

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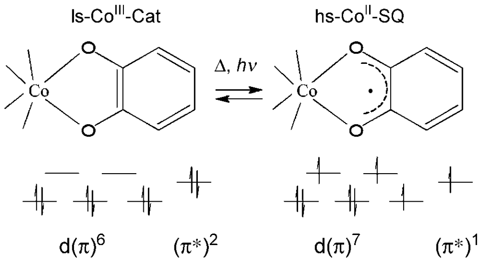
Valence tautomerism (VT) defines reversible interconversions between two or more redox isomers. It is established that these interconversions can be stimulated by temperature and light irradiation.[1] For example, the diamagnetic [Co^{III}-(Me_2tpa)(DBCat)]$PF_6 \cdot C_6H_5CH_3$ complex (**1**) (Me_2tpa = bis(6-methyl-(2-pyridylmethyl)) (2-pyridylmethyl)amine, DBCat = 3,5-di-*tert*-butylcatecholato) was found to undergo a thermally induced interconversion in the solid state yielding the redox isomer characterized by the high-spin Co^{II}-semiquinonato (hs-Co^{II}-SQ) charge distribution (see Scheme 1).[2,3] The observed transition can be formally described as the result of an entropy-driven intramolecular electron transfer involving the donor catecholato and the cobalt(III) acceptor. At cryogenic temperatures, laser irradiation of the solid compound at 904 nm, where a ligand-to-metal charge transfer (LMCT) occurs, was found by bulk magnetic measurements[2] to induce the same process, affording the hs-Co^{II}-semiquinonato species as a metastable phase in 90% yield with a rather long lifetime (two weeks at 9 K).

Soft X-ray absorption spectroscopy (XAS) is an element-sensitive synchrotron-based technique and provides a powerful tool to study the electronic and chemical structure of a specific atom and its coordination environment. It is particularly powerful in the magnetic study of 3d metal complexes.[4] With the additional asset of very high detection sensitivity, XAS has been effectively used in the characterization of systems with multiple quasi degenerated electronic states,[5] including very diluted and nanostructured systems.[6] We have found that for **1** this technique not only yields this important information, but also intrinsically provides the perturbation for inducing interconversion between the two redox isomers. This is an unprecedented result and we believe it to be particularly important for the study of all the complexes exhibiting photochromism.



Scheme 1. The two different electronic configurations involved in VT process.

Figure 1 shows the temperature dependence of the cobalt L_3-edge X-ray absorption spectra of **1** (the $L_{2,3}$ spectra are shown in Figure S1 of the Supporting Information). The spectra were obtained with a X-ray flux of 10^8 photons s^{-1} on

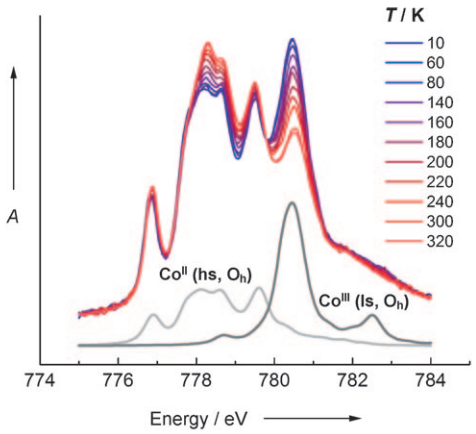


Figure 1. Temperature dependence of the normalized L_3-edge X-ray absorption spectra of **1**, acquired with a low X-ray photon flux on the sample. The underlying light gray and dark gray curves show the theoretical spectra expected for pure Co^{II} and Co^{III} states, respectively (see text for details).

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the sample and were simulated in the framework of a ligand-field multiplet (LFM) approach[7,8] using the parameters obtained for the same system at K-edges.[9] This approach demonstrated the predominant presence at low temperature (10 K) of low-spin (ls) Co^{III} species with a minor fraction of hs-Co^{II} species whereas the opposite situation is observed at high temperature (300 K). As a whole, these results confirm the occurrence of the aforementioned entropy-driven conversion of ls-Co^{III} into hs-Co^{II} on increasing temperature and the presence of an unavoidable temperature-independent fraction of hs-Co^{II} arising from surface defects.[10]

The temperature dependence of the spectra of the same sample after 1 h irradiation with 904 nm laser light at 9 K and under the same X-rays flux of 10^8 photons s^{-1} is shown in the upper panel of Figure 2. At the lowest temperature a large increase of the amount of the hs-Co^{II} species compared to the non-irradiated sample is clearly evident. Raising the temperature in the range 10–80 K, the amount of the optically induced Co^{II} metastable phase decreases because of the thermally activated relaxation to the electronic ls-Co^{III} ground state. Heating the sample above 100 K the Co^{II} concentration increases because of the occurrence of the entropy driven interconversion process.

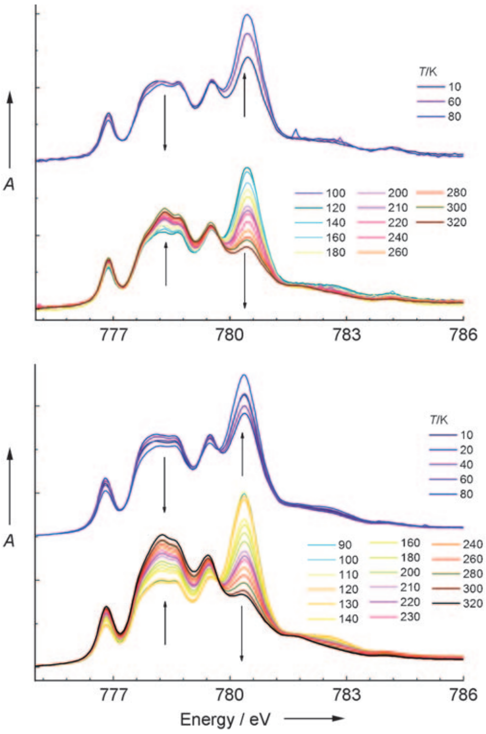

Figure 2. Upper panel: Temperature dependence of the normalized X-ray absorption spectra of **1**, acquired with a low X-ray photon flux on the sample after 1 h of 904 nm laser-light irradiation. Lower panel: Temperature dependence of the normalized X-ray absorption spectra of **1**, acquired with a high X-ray photon flux on the sample without laser irradiation.

A long exposure to the beam shows that at low temperature a weak but detectable interconversion from Co^{III}-catecholato species into Co^{II}-semiquinonato may occur even in the absence of laser light irradiation. For this reason, having excluded any radiation damaging processes, we investigated the effect of an increase of the soft-X-ray photon flux on the electronic structure of **1**. The X-ray density of the irradiating beam was raised to 10^{10} photons s^{-1}, yielding the temperature-dependent XAS spectra shown in the lower panel of Figure 2. The temperature dependence of the spectra recorded from un-exposed sample in high X-ray photon-density regime is qualitatively identical to that observed after the 904 nm laser light irradiation and under lower X-ray photon density.

The close similarity observed between the two patterns holds also at a quantitative level, as is clear by comparing the temperature dependence of the hs-Co^{II} fraction undergoing VT equilibrium in the two cases (Figure 3, upper panel). A reasonable fit for the spectrum at 9 K was obtained assuming a linear combination of 30% ls-Co^{III} and 70% hs-Co^{II} components in simulated spectra (Figure S2, Supporting Information). However, this analysis is strongly affected by the presence of the redox inactive hs-Co^{II} contribution, which may depend on sample preparation. To get rid of this contribution we assumed that at each temperature the XAS spectrum is the result of a linear combination of the spectra

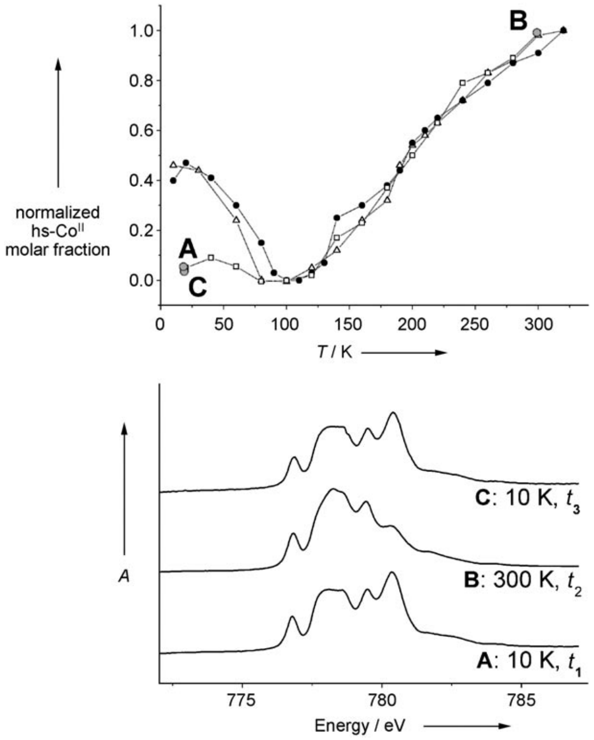

Figure 3. Upper panel: Temperature dependence of the hs-Co^{II} fraction undergoing VT equilibrium for a sample measured under a 10^8 X-rays photons s^{-1} flux in the dark (squares), and after 1 h of 904 nm laser-light irradiation (triangles). The filled gray circles labeled **A**, **B**, and **C** are extracted from the spectra in the lower panel. The filled black circles represent the fraction of hs-Co^{II} obtained in the dark under a 10^{10} X-ray photons s^{-1} flux. Lower panel: Evidence of the reversibility of the soft-X-ray-induced valence tautomeric interconversion: L_3-edge XAS spectra of complex **1** at 10 K before (**A**) and after (**C**) a complete thermal cycle up to 300 K (**B**) (time scale $t_1 < t_2 < t_3$).

recorded at 300 K and 80 K, which are considered as the limiting compositional cases corresponding to 100 % and 0 %, respectively, of the redox-active hs-Co^{II}-semiquinonato phase. This treatment provides a more reliable estimation of the photoinduced fraction at low temperature obtained by 904 nm irradiation with low X-ray flux (equal to 40 % of the redox-active part of the sample). The conversion efficiency is the same when using only high X-Ray flux irradiation. On the other hand, the temperature at which the hs-Co^{II}-semiquinonato charge distribution completely relaxes to the Co^{III}-catecholato one is, within experimental error, comparable in the two cases confirming the efficiency of soft X-rays in promoting the VT interconversion. The reversibility of the X-ray-triggered conversion is demonstrated by the comparison of the temperature dependence of the hs-Co^{II} molar fraction obtained in different experimental conditions (as shown in the upper panel of Figure 3 and in Figure S3, Supporting Information).

The present results clearly demonstrate that soft X-rays trigger the same process as 904 nm laser light, that is, they are capable of inducing an intramolecular electron transfer. The process is totally reversible, as demonstrated by the comparison of the spectra recorded at 10 K before and after a complete thermal cycle up to 300 K (see lower part of Figure 3). The sample began showing photoinduced degradation only after 600 spectra (corresponding to more than 24 h) have been recorded on the same spot of the sample at high flux.

Even though the detailed mechanism by which soft X-rays promote the VT interconversion in **1** is not clear yet, we attribute it to the presence of secondary electrons having energy in the range of the LMCT transition.[11] The interconversions induced by hard X-rays reported up to date,[10,12–15] involving manganites,[13] iron spin crossover,[12] and polycyanometallates,[10,14,15] have been attributed to the scattering of secondary electrons produced by a remote ionization.[4,12] In the case of soft X-ray photo-absorption, the non-radiative decay through Auger and Coster–Kronig electrons is expected to be higher,[11c] resulting in a higher efficiency of the secondary electrons produced by inelastic scattering compared to those produced by hard X-rays. In principle, this makes soft X-rays more efficient in promoting the redox isomerism. However, the larger number of secondary electrons can easily induce irreversible damage of the system, making the X-ray-induced transitions harder to detect. In this framework, the observed behavior of **1** indicates that this molecular complex is highly robust, which allowed us to monitor the occurrence of soft X-ray-induced VT with no irreversible radiation damage. This result has to be compared to an earlier reported soft X-ray-induced spin-crossover transition in a molecular complex, which was associated with significant sample damage caused by the photon beam. It was also rather unclear if the latter process could be associated with the observed spin transition.[16] This problem can be excluded in the present case.

In conclusion, these results confirm that soft X-rays can be used as a probe for obtaining information about the electronic properties of 3d metal ions and indicate that they can act as a powerful external perturbation, like those provided by temperature, pressure, magnetic field, and optical photons. In this case, indeed, soft X-rays play the role of excitation source in promoting the transition to metastable electronic states. This can be very important for the investigation of all the metal complexes showing photochromic behavior. The result reported herein constitutes, to our knowledge, the first example of a completely reversible soft-X-ray-induced electron transfer in a molecular complex.[17]

Experimental Section

The synthesis of **1** has been carried out following a reported procedure.[3] The compound has been characterized by means of elemental analysis and standard magnetometric techniques (see Supporting Information). The X-rays absorption spectra have been acquired at the ID08 beamline located at the European Synchrotron Radiation Facility (ESRF) in Grenoble, France. The X-ray absorption spectra have been acquired from a drop-cast sample of **1** from toluene, inserted in a special holder designed to allow sample irradiation with both an X-ray beam and a CW 904 nm laser beam. The power of the 904 nm laser on the sample was 10 mW cm^{-2}. The holder was inserted in a cryostat working in the 6–320 K temperature range, and the X-ray photon flux onto the sample was tuned by selecting the opening of the slits downstream of the Apple II undulator of ID08. The spectra were recorded in total electron yield detection mode. The theoretical spectra for Co^{II} and Co^{III} based species have been simulated within the framework of ligand-field multiplet (LFM) calculations with the same set of parameters as those determined for the calculation of the pre-edge at Co K-edges in Ref. [9].[7,8]

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