First insights into the structure of tri-nuclear µ-oxo iron complexes by RIXS spectroscopy

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The understanding of the operating mode of non-heme enzymes such as methane monooxygenase and ribonucleotide reductase is currently a major challenge because this knowledge is prerequisite for biomimetic oxidations of hydrocarbons employing dioxygen. Theoretical and experimental studies on synthetic model complexes have provided insight into catalytic cycles, reactive intermediates, competing energy profiles and product distributions [1]. However, these model complexes are often limited by low selectivities and turnover numbers, poor stability, stoichiometric amounts of oxidants, or difficult variation of the ligand system. Thus, there is still a need for novel non-heme iron complexes, whose ligand systems can be varied easily in order to improve the catalytic properties.

Trinuclear µ-oxo iron complexes with a Fe₃O group are particularly suited for this purpose [2]. We chose complexes with pyridine dicarboxylate ligands, in which the carboxyl group is separated from the pyridine moiety by an alkyl spacer of variable length, in order to vary nuclearity, stability and catalytic properties. A sketch of the investigated complexes 401, 464, 469 and 476 is given in figure 1. Since these complexes do not crystallize, structural characterization can not be carried out by X-ray diffraction. In frame of conventional X-ray absorption spectroscopy (XAS) experiments, all complexes of figure 1 exhibit similar structural parameters. From the EXAFS analyses, nothing can be said about the number of coordinating chlorine ligands, which are found in elemental analyses. Moreover, XANES measurements and prepeak evaluation indicate an octahedral coordination of the iron center, but the distortion of the octahedral symmetry can not be determined [3]. Both questions were attempted to answer by 1s2p-RIXS (Resonant Inelastic X-ray Scattering) spectroscopy carried out at beamline W1 at HASYLAB. The sensitivity of X-ray emission to d-electron densities should allow to identify the effect of electron drawing chlorine ligands. Because core-hole broadening can be strongly reduced by this method, it allows a more accurate analyses of prepeaks [4]. The 1s2p RIXS planes of the complexes 401, 464, 469 and 476, with alkyl chain lengths from n=2 to n=5 carbon atoms are presented in figure 2. In these plots, the intensity of the scattered radiation is plotted against the incident excitation and emitted radiation energy. In figure 3, the prepeaks of the investigated samples as obtained by conventional K-edge XANES spectroscopy and by integration over the Kβ₁,3 emission line are compared to each other. The broadening of the signal in the RIXS-deduced spectra is significantly reduced, thus allowing a more thorough interpretation of the pre-edge signal, which originates from a 1s → 3d transition. The energy position and intensity are strongly dependent on spin state, oxidation state and geometry [5]. In general, the total intensity of the transition shows an increase with decreasing coordination number due to the loss of inversion symmetry of the coordination sphere of the iron site [6]. Therefore the five samples can be ordered according to their degree of symmetry. The sample 476 shows the highest degree of symmetry, sample 469 has the largest distortion of the octahedral symmetry, while 401 and 464 can be found in between. The octahedral distortion is thus correlated

<table>
<thead>
<tr>
<th>Complex</th>
<th>469</th>
<th>401</th>
<th>464</th>
<th>476</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkyl chain length (n)</td>
<td>2</td>
<td>3</td>
<td>4</td>
<td>5</td>
</tr>
</tbody>
</table>

Figure 1: Structure of trinuclear µ-oxo iron complexes with variable length of the alkyl chains (Ar = pyridine).
with the length of the applied alkyl chain length. Remarkably, the prepeak in sample 469 shows a shoulder towards smaller energy. Detailed data analyses is in progress and the information contained in the 1s2p RIXS spectra concerning the electronic structure and its changes by coordinating chlorine will be analyzed with further measurements, using well defined, structurally related reference samples and calculations.

References