Soft X-ray emission and absorption—a comparative study on the sensitivity to oxidation state and ligand environment of transition metal complexes


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Abstract

In order to understand the function of transition metals, which are a necessary part of many catalytic cycles, it is necessary to obtain information about oxidation states, ligand environment, and local structure surrounding the metal centers. L-Edge X-ray absorption spectroscopy, which probes the unoccupied 3d levels, has been shown to be a sensitive probe of the oxidation and spin state of transition metal sites. As soft X-ray fluorescence (SXF) instead probes the occupied states, an investigation of how this complementary technique can be used to probe transition metal centers was conducted and the results are presented here. SXF is found to be very sensitive to ligand environment and relatively insensitive to electronic geometry and metal oxidation state. Potential applications of this technique to systems such as metalloproteins and manganese–lithium batteries are discussed. © 1998 Published by Elsevier Science B.V. All rights reserved

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1. Introduction

Transition metals are a necessary part of many catalytic cycles. They play a major role in biological redox reactions (e.g. iron in nitrogenase and manganese in photosystem II) as well as in material science applications. For example, manganese has been proposed as a less toxic and less expensive alternative to nickel-based electrodes in rechargeable batteries [1]. In order to understand these systems, it is necessary to obtain information about oxidation states, ligand environment, and local structure surrounding the metal centers.

Much effort has gone into using X-ray absorption spectroscopy (XAS) to study these systems, taking advantage of the element-specific nature of this technique. Both 'soft' (100–1200 eV) and 'hard' (1200–12000 eV) XAS have been used to investigate a variety of metal centers. The benefit of using 'soft' X-rays to study 3d transition metals is the longer core-hole lifetime of the L-edge transitions which occur in this region, compared to the corresponding K-edges in the 'hard' X-ray regime. This decrease in linewidth leads to better-resolved features in the spectra. L-Edge
XAS, which probes the unoccupied 3d levels, has been shown to be a sensitive probe of the oxidation and spin state of transition metal sites in proteins [2–4]. As soft X-ray fluorescence (SXF) instead probes the occupied states, an investigation of how this complementary technique can be used to probe transition metals was conducted and the results are presented here.

2. Experimental

Soft X-ray absorption experiments were performed on beamline 6.3.2 at the Advanced Light Source. This is a bend magnet beamline with a Hetttrick-Underwood type monochromator capable of high resolution, as has been previously described [5]. A 1200 lines mm⁻¹ grating with an exit slit of less than 20 μm resulted in a resolving power (E/ΔE) of better than 1200 at the Mn L-edge. Energy calibration was checked during the measurements by ensuring that the L₃ peak in a MnF₂ absorption spectrum occurred consistently at 639.36 eV.

The absorption was monitored by collecting the total current from the sample as a function of excitation energy. The incident intensity (I₀) of the X-ray beam was recorded as the current from either a gold mesh in the beampath or the refocusing mirror. Spectra were recorded over a 30 eV range with a step size of 0.05 eV. The spectra were divided by I₀ and normalized to unit intensity at the LII peak. All samples were finely powdered and pressed into indium metal. The sample slide was then mounted perpendicular to the incoming X-ray beam.

Soft X-ray fluorescence spectra were recorded on beamline 8.0 at the Advanced Light Source. This is an undulator beamline with a spherical grating monochromator, as has been previously described [6]. A 925 lines mm⁻¹ grating was used to monochromatize the excitation energy for these measurements and the energy was calibrated by setting the LII peak of MnF₂ to 639.36 eV. Throughout the series of Mn emission scans, the monochromator and undulator were fixed at 672.58 eV and 23.78 mm, respectively. The incident beam intensity was monitored as the current from a gold mesh in the beampath.

The soft X-ray fluorescence endstation [6] consists of a Rowland circle type emission spectrometer with a fixed 100 μm entrance slit and a 1500 lines mm⁻¹ grating mounted on a 10 m Rowland circle. The X-ray fluorescence is refocused onto a multichannel plate area detector, enabling the entire emission spectrum to be obtained without scanning the detector. Emission spectra were calibrated relative to the LII emission of MnO [7]. Spectra were normalized to unit intensity at the LII peak. Samples for emission measurements were finely powdered, pressed into pellets, and mounted in the chamber at 22° to the incoming beam.

Mn(acac)₂ (where acac is acetylacetonate), Mn(acac)₃, Mn(pc) (where pc is phthalocyanine), Mn(pc)Cl, MnF₂, and MnCl₂ were used as obtained from Aldrich Chemical Company. λ-MnO₂ was from Covalent Associates, Inc. The MnO and MnS samples were provided by C.R. Horne and K. Lawniczak-Jabionska, respectively.

3. Results and discussion

The soft X-ray absorption and emission spectra of two oxidation state pairs are shown in Fig. 1. The Mn centers in Mn(II)(acac)₂ and Mn(III)(acac)₃ have oxygen ligation with tetrahedral and octahedral geometry, respectively. The Mn in Mn(II)(pc) is square planar with nitrogen ligation. Mn(III)(pc)Cl adds a chloride ligand to the ligation sphere and the resulting complex is square pyramidal. In both cases, the X-ray absorption spectrum of Mn(II) is strikingly different from that of Mn(III) (Fig. 1, left). The LIII peak occurs at 639.35 eV and 639.37 eV for the Mn(II)(acac)₂ and Mn(II)(pc), respectively. Both spectra have around 11.3 eV separation between LIII and LII and have similar multiplet structure, in spite of the differences in geometry and ligation. The Mn(III) spectra occur about 1.4 eV higher than the corresponding Mn(II) spectra, are much broader, and have a more equal distribution in intensity between the LIII and LII regions of the spectrum. This increase in energy, decrease in the ratio of LIII to LII, and increase in broadness with increasing oxidation state has been observed in Mn complexes previously [8]. These spectral differences can be used to determine the average oxidation state in an unknown manganese compound [3]. Although large differences in the ligand coordination can cause changes in electronic geometry and spin state which are often readily observable in
the absorption spectra [8], relatively small differences appear as a result of minor changes in ligation. Determining the relative percentages of oxygen or nitrogen, for example, can be quite difficult.

In contrast to X-ray absorption, the X-ray emission spectra of complexes with different oxidation states but similar ligation are remarkably similar in both the broadness and the energy position of the L_α and L_β peaks, neither of which show resolved multiplet features (see Fig. 1, right). The L_β peak occurs at 648.2 eV and 649.0 eV for the Mn(II)(acac)_2 and Mn(II)(pc) spectra, respectively, 9–10 eV higher in energy than the L_α peak. An increase to a higher oxidation state results in no change to the L_β region of the Mn(III)(acac)_2 and a slight increase in broadness for the Mn(III)(pc)Cl. The major difference between the Mn(II) and Mn(III) spectra with similar ligation is not a change in energy position but instead an increase in

Fig. 2. Spectral parameters of Mn emission spectra. Left: the energy of the zero crossings for the first-derivative Mn emission spectra is plotted versus the average atomic group number of the ligands. Data from complexes with oxidation states of Mn(II) to Mn(IV) are shown. Right: the inverse linear dependence of the L_α/L_β ratio on the group number of the ligands is shown for a series of Mn(II) complexes.
Table 1
Spectral parameters of Mn compounds

<table>
<thead>
<tr>
<th>Ligand group number</th>
<th>Compound</th>
<th>$L_{\alpha}/L_{\beta}$ ratio</th>
<th>First zero crossing (eV)</th>
<th>Second zero crossing (eV)</th>
<th>Third zero crossing (eV)</th>
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<tr>
<td>5</td>
<td>Mn(II)(pc)</td>
<td>1.57</td>
<td>640.70</td>
<td>645.07</td>
<td>648.97</td>
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<td>5.5</td>
<td>Mn(III)(pc)/Cl</td>
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<td>640.64</td>
<td>645.14</td>
<td>649.03</td>
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<td>6</td>
<td>Mn(II)(acac)$_2$</td>
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<td>637.75</td>
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<td>648.50</td>
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<tr>
<td></td>
<td>Mn(III)(acac)$_3$</td>
<td>1.43</td>
<td>637.75</td>
<td>644.13</td>
<td>648.50</td>
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<td></td>
<td>Mn(II)O</td>
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<td>637.61</td>
<td>644.13</td>
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<tr>
<td></td>
<td>λ-Mn(IV)O$_2$</td>
<td>3.13</td>
<td>638.08</td>
<td>644.13</td>
<td>648.97</td>
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<td>Mn(II)S</td>
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<td>–</td>
<td>–</td>
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<td>&lt; 7</td>
<td>Mn(II)Cl$_2$·H$_2$O</td>
<td>1.05</td>
<td>638.38</td>
<td>644.90</td>
<td>648.97</td>
</tr>
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<td>Mn(II)F$_2$</td>
<td>0.78</td>
<td>638.08</td>
<td>644.77</td>
<td>648.80</td>
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</table>

*Zero crossings are reported for the first derivative of the Mn emission spectra.

the ratio of the integrated area of the $L_{\alpha}$ region divided by that of the $L_{\beta}$. In order to precisely determine and compare the energies of the spectral features, the zero crossings of the first derivatives of the emission spectra were measured and are tabulated in Table 1. For ligation by (acac), the energies of the emission spectra are virtually unaffected by a change in oxidation state and the accompanying change in geometry. Similarly, in the case of the (pc) complexes, the energy differences of the zero crossings are very small (less than 0.1 eV). In contrast, there is an around 3 eV difference between the first zero crossing for Mn(acac)$_2$ and Mn(pc). In addition, the $L_{\alpha}/L_{\beta}$ ratio increases more upon changing ligation from oxygen to nitrogen than from increasing the oxidation state, as summarized in Table 1. This relative insensitivity of the energy of Mn emission spectra to oxidation state and geometry, and sensitivity of both the energy and the $L_{\alpha}/L_{\beta}$ ratio to the ligand environment is further demonstrated in Fig. 2 and Table 1.

Mn $L$-emission spectra were recorded for two sets of Mn complexes. The first group had oxygen ligation and varying Mn oxidation states while the second was a series of divalent Mn complexes with varying ligation. The $L_{\alpha}/L_{\beta}$ ratios and the energies of the zero crossings from the first derivative of the emission spectra are tabulated in Table 1 and plotted versus the group number of the ligands to the manganese in Fig. 2 (emission spectra not shown). In the case of the four Mn complexes with oxygen ligation: Mn(II)(acac)$_2$, Mn(II)O, Mn(III)(acac)$_3$, and λ-Mn(IV)O$_2$, the $L_{\alpha}$ and $L_{\beta}$ peaks maintain a similar energy position throughout the oxidation state range. The spectra do, however, show an increase in both broadness and branching ratio with increasing oxidation state. Although the second two zero crossings are relatively independent of ligation for the series of Mn(II) complexes, an increase in broadness in the $L_{\alpha}$ region (by around 3 eV) is seen for ligands with an atomic group number of 6 and higher. This is shown by the lower energy position of the first zero crossing for these spectra. In addition, a strong correlation ($r^2 = 0.998$) is seen between the $L_{\alpha}/L_{\beta}$ ratio and the atomic group number of the ligands to the manganese (see Fig. 2, right). Increasing the group number from 5 to 7 results in a linear decrease in the $L_{\alpha}/L_{\beta}$ ratio. This inverse dependence on the ionicity of the compound has been noted previously in copper complexes [9].

Although atomic multiplet calculations can successfully simulate manganese soft X-ray absorption spectra [3,8], the application of these calculations to soft X-ray emission spectra measured with above threshold excitation is more difficult. Efforts to use these and other types of calculations to simulate manganese soft X-ray emission spectra and reproduce the experimental findings reported here are currently in progress.

4. Conclusions

Mn $L$-edge absorption is known to be a sensitive probe of both oxidation and spin state. In contrast, $L$-edge emission has been shown here to be very sensitive to ligand environment and less sensitive to the electronic geometry and oxidation state of the
manganese ion. The linear dependence of the $L_\alpha/L_\beta$ ratio on the group number of the ligands to the manganese suggests a method of determining the ligand environment of a transition metal of known oxidation state. This is especially exciting for metalloproteins in cases where the percentage of oxygen versus nitrogen ligation is not known. Other X-ray techniques such as EXAFS are not sensitive enough to distinguish between two elements of such close proximity in the periodic table as oxygen and nitrogen. In addition, the $L_\alpha/L_\beta$ ratio offers a probe of the covalency of the complex. As mentioned earlier, rechargeable batteries based on LiMn$_2$O$_4$ electrodes have been suggested as an alternative to the traditional nickel-based systems. Substitutions of other metals in small quantities have resulted in an improvement in the cycling properties of these materials [10,11]. However, the relationship between metal substitution and cycling enhancement is not well understood. By measuring the X-ray emission spectra on these components, it will be possible to probe the occupied states to gain an understanding of the difference in performance as dependent on electrode composition. These two examples show the potential of soft X-ray emission to be a powerful tool in examining transition metal catalytic systems.

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