

Supporting Information:

Experimental and Computational X-ray Emission Spectroscopy as a Direct Probe of Protonation States in Oxo-Bridged Mn^{IV}-Dimers Relevant to Redox-active Metalloproteins

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Geometric Details

Chart S1. Geometric details for the optimized geometries of **1**, **2**, **3a** and **3b** in comparison to EXAFS data from Ref. 1, given in italics where applicable.

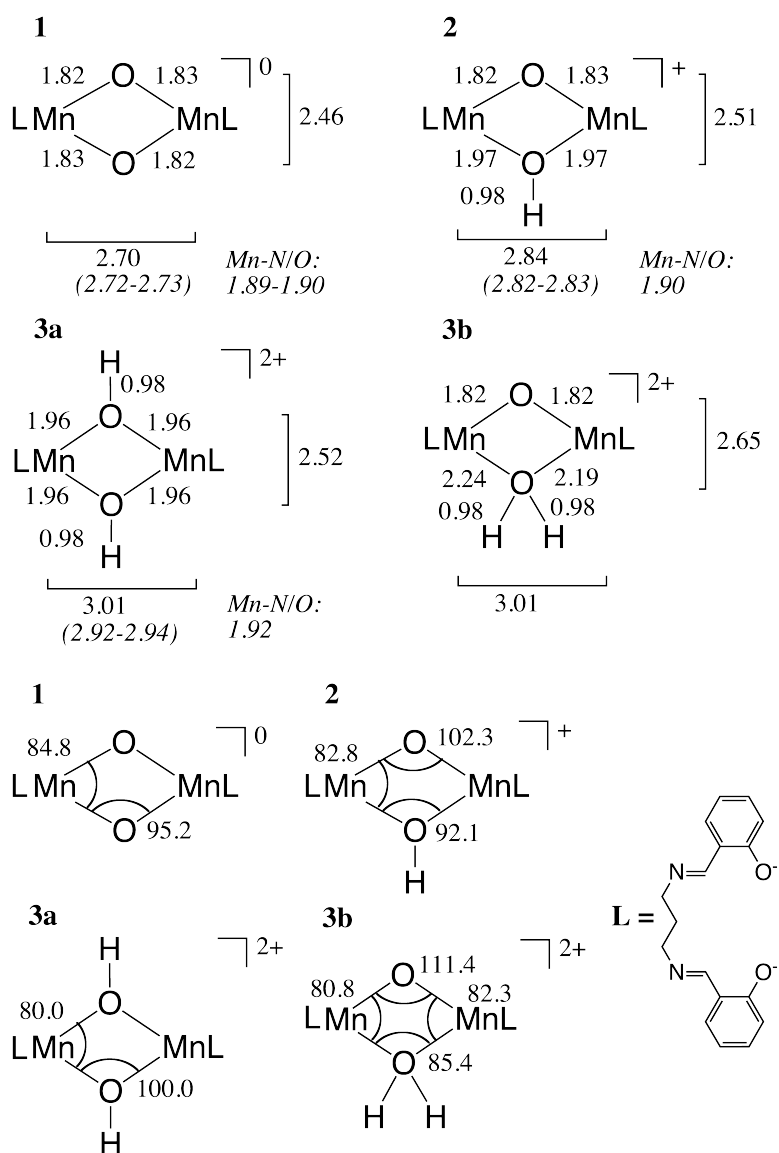


Figure S1. Experimental XES valence-to-core difference spectra of the *salpn* dimer series. The red dotted line corresponds to the difference spectrum of compound 2 with compound 1, the blue dashed line to the difference spectrum of compound 3 with compound 1. The changes in the $K\beta''$ region are the most important, with the intensity for (3-1) at ~ 6520 eV approximately twice the intensity of that for (2-1). The shoulder to the $K\beta_{2,5}$ peak at ~ 6530 eV is represented as positive difference intensity of the same magnitude, whereas the main peak is represented with negative difference intensity.

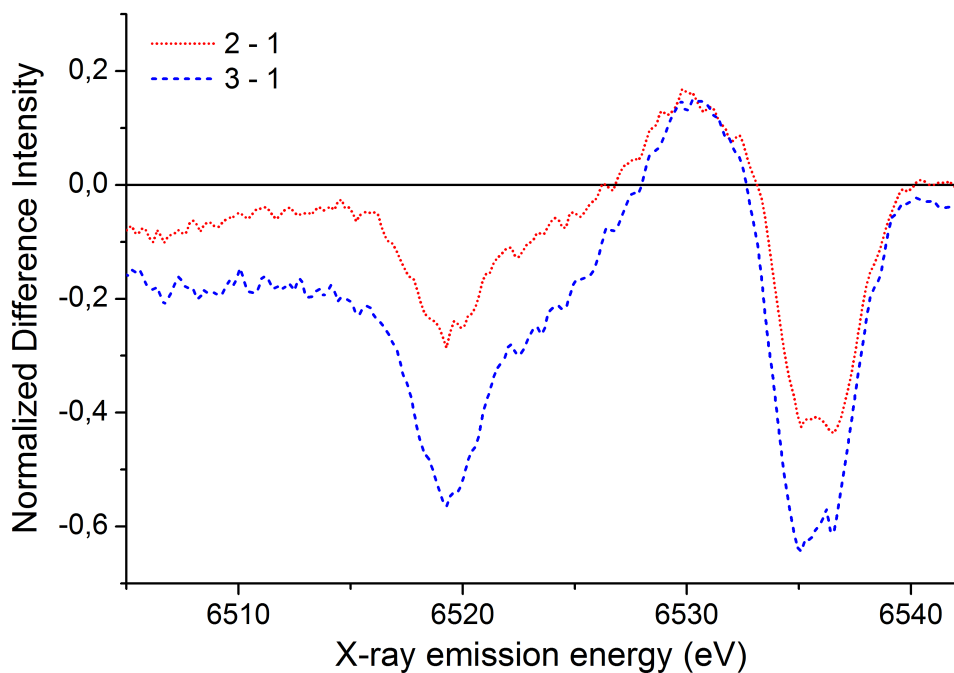
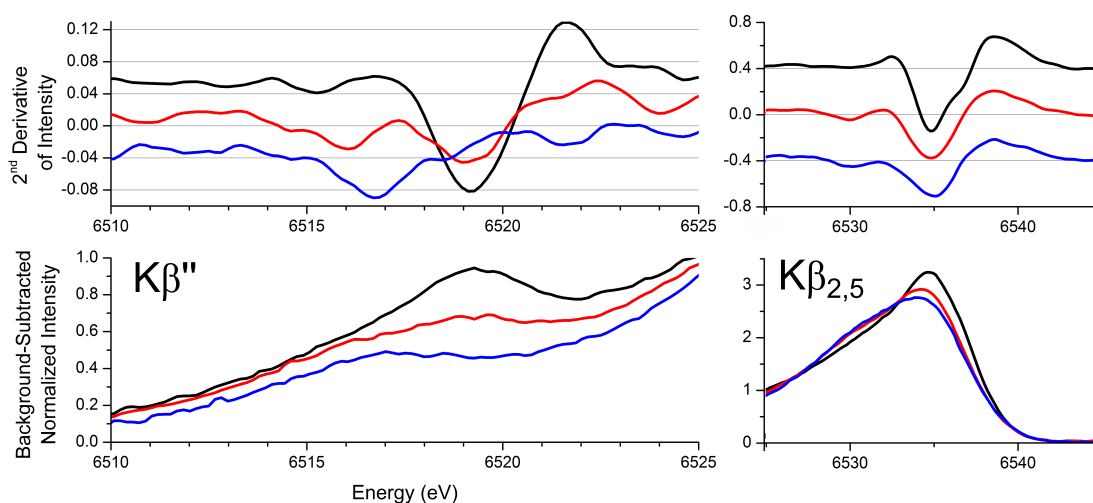


Figure S2. Background-subtracted normalized valence-to-core regions (bottom) and their 2nd derivatives (top) for complexes 1 (black, shifted up by 0.4 units on the y-axis), 2 (red, at 0 on the y-axis), and 3 (blue, shifted down by 0.4 units on the y-axis). The 2nd derivatives were generated from the 1st derivatives, with a 10-point (~ 1.45 eV) Savitzky-Golay smooth of 2nd order in each derivative step.



Input file examples for the calculation of valence-to-core X-ray emission spectra with a one-electron approach

The implementation of the one-electron approach has been described in Ref. 2, and the calculation setup used in this work was introduced in Ref. 3. This is a description of an input file for an XES valence-to-core calculation with the ORCA program package.⁴ Each keyword can be modified according to the requirements of the calculation; please refer to the ORCA manual or the ORCA JumpStartGuide for other keywords (invoking other functionals, basis sets, solvent models, relativistic corrections etc.). The latest release and the manual can be found at

<http://www.ccc.mpg.de/downloads>

or

www.ccc.mpg.de/forum/portal.php

```
! SP BP def2-TZVP(-f) ZORA COSMO(CH2Cl2) grid4 NoFinalGrid SOMF(1X)
% xes
  coreorb 0,0,1,1
  orbop 0,1,0,1
  doSOC true
  coreorbSOC 0,1,2,3
end
* xyz 0 7
...
*
```

The exclamation point (!) indicates the start of a 'simple input line'.

SP: keyword for a single point calculation

BP: selects the functional BP

def2-TZVP(-f): selects the basis set def2-TZVP(-f)

ZORA: invokes the 0th order relativistic approximation

COSMO(CH₂Cl₂): models a solvent with the properties of CH₂Cl₂ using COSMO⁵.

Grid4, NoFinalGrid: specifies the integration grid size settings for the calculation. Increasing the grid will make the calculations more accurate, but also more expensive in terms of computational costs. Refer to the manual for default values.

SOMF(1X): invokes the use of the spin orbit mean field approximation for the SOC operator, as discussed in Ref. 3.

The percentage sign (%) indicates the start of a 'methods block', which is terminated with an **end**.

xes: specifies the block for the calculation of X-ray emission spectra

The next two keywords and the numbers specifying the core orbital properties depend on each other:

coreorb 0,0,1,1: specifies the core orbitals

orbop 0,1,0,1: specifies the orbital operators for the core orbitals

Here, the core orbitals **0** (on Mn1) and **1** (on Mn2) with the operators **0,1** (Mn1) and **0,1** (Mn2) are chosen. Operator 0 refers to α electrons; operator 1 refers to β electrons. The core orbitals can be recognized from the output of a previous calculation (for instance, a geometry optimization with the 'largeprint' keyword in the simple input line). For transition metal ions with only light C/N/O/H atoms in the ligand, they are usually the energetically lowest lying ones. For molecules with heavier halides however, the 1s orbitals of the metals can have higher energies than those of the halides.

doSOC true: use spin-orbit coupling

coreorbSOC 0,1,2,3: specifies the spin-orbit coupled core orbitals

The coordinates are given after a line specifying

*xyz 0 7

where xyz indicates the use of Cartesian coordinates and the numbers 0 and 7 refer to the total charge and multiplicity of the molecule, respectively. The coordinates (...) end with a second asterisk *.

The spectra can be plotted with the orca_mapspc program, resulting in a file.dat file (line spectrum) and a file.stk file (stick spectrum):

```
orca_mapspc file.out XESSOC -x05730 -x16485 -w2.0 -n4000
```

where **file.out** is the output file of the XES calculation; **XESSOC** specifies the type of spectrum to plot (use XES if you did not use SOC); **-x0** and **-x1** give the energy axis range (here 5730 eV to 6485 eV, remember to shift the calculated spectra by 59.2 eV for the setup above); **-w2.0** specifies the artificial broadening used to get the line spectrum in the **file.dat** file from the transitions stored in the **file.stk** file; **-n** specifies the number of points for the line spectrum, here 4000.

Table S1. Experimental and calculated areas for the reference monomer data used in the correlation plot Figure 8.

Compound		Experiment		Calculation
#	Name	Area	std. dev.	Area
1	[Mn(II)(acac) ₂]	14.88	1.25	8.50
2	[Mn(II)(^{tert} Bu ₃ terpy) ₂] ²⁺	15.55	0.85	8.49
3	[Mn(II)(terpy)Cl ₂]	16.49	0.64	7.93
4	[Mn(II)(tolyterpy) ₂] ²⁺	16.90	1.69	8.44
5	[Mn(II)(tpa)(NCS) ₂]	16.13	2.18	8.56
6	[Mn(II)(^{tert} Bu ₃ terpy)(N ₃) ₂]	20.96	2.19	9.83
7	[Mn(II)(CF ₃ CO ₂) ₂ (terpy)(H ₂ O)]	17.62	0.82	7.42
8	[Mn(II)(terpy)(NO ₃) ₂ (H ₂ O)]	16.47	1.19	7.13
9	[Mn(III)(acac) ₃]	24.66	0.91	11.60
10	[Mn(III)(bpea)(N ₃) ₃]	21.25	0.95	12.10
11	[Mn(III)(salen)Cl]	27.56	1.28	15.50
12	[Mn(III)(terpy)Cl ₃]	18.42	0.99	10.00
13	[Mn(III)(terpy)(N ₃) ₃]	25.67	1.74	12.70
14	[Mn(III)(tolyterpy) ₂] ³⁺	30.29	1.48	13.10
15	[Mn(IV)(Me ₃ -tacn)(OMe) ₃] ⁺	24.59	1.06	15.50
1	[Mn(IV)(μ-O) ₂ (salpn) ₂]	45.40	1.60	19.13
2	[Mn(IV)(μ-O)(μ-OH)(salpn) ₂] ¹⁺	41.28	0.79	19.76
3	[Mn(IV)(μ-OH) ₂ (salpn) ₂] ²⁺	43.94	1.01	18.70

The standard deviations listed here result from all fits generated and were used in Figure 8 to display the error bars. An additional error of ±5% is estimated to occur from differences in background subtraction and data normalization.

References

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