Electronic Supplementary Information

Can oxidation states and protonation pattern of oxomanganese complexes be *recognized* from their structures?

Arturo Robertazzi,[a] Artur Galstjan,[a] and Ernst Walter Knapp*[a]
a: Freie Universität Berlin, Institute of Chemistry & Biochemistry, Fabeckstr. 36a, D-14195 Berlin, Germany

DFT vs. Experiment: test calculations.

As mentioned in the computational details, it has been shown that B3LYP combined with a basis set slightly smaller than that used in this work (*e.g.* LACVP basis set on the metal, 6-31G(d) for oxobridge oxygens, 6-31G for other oxygens and nitrogens, 3-21G for carbons and hydrogens) can very well reproduce the structural parameters of oxomanganese complexes.[1] In addition, B3LYP/LAVCP* has been recently employed to study the new crystal structure of the Mn_4Ca cluster in PSII.[2] Thus, we are confident that the basis set employed in this work, LAVCP**, can properly reproduce the structural parameters of the studied oxomanganese complexes. Yet, we have performed some test calculations and have compared our data with experimental and/or previous theoretical studies. Data are collected in table S1. Complexes 1-3 are oxomanganese compounds studied by Batista et al using DFT.[1] Agreement with experiments and with Batista's work is excellent. Further discussion is, however, needed for the dMn complexes XUWSEN and QOSMOA (Table S1). In the former case, the authors claim that the compound bears two hydrogens on the oxobridge oxygens.[3] However, no crystal data are available supporting this statement. We believe that the structure reported by the authors is in fact that of a complex with no hydrogens on the bridging oxygens. Indeed, excellent agreement between DFT and experiment is achieved when no hydrogens were added on the oxobridge oxygens. In case of QOSMOA,[4] the authors have faced serious problems during the crystallization as the determination of the compound was "handicapped by the combination of a poorly diffracting sample, disorder, seen as diffuse scattering on the diffractograms". Yet, the agreement between the crystal structure and the structure obtained from geometry optimization with DFT is fair.

Table S1. Comparison between DFT and experiment on the studied oxomanganese compounds. Mn-Mn and ∑Mn-O (the average of all four Mn-O distances) are displayed.

	Expt.		Previous DFT studies[a]		This work	
	Mn-Mn	∑Mn-O	Mn-Mn	∑Mn-O	Mn-Mn	∑Mn-O
Complex 1[a]	2.72	1.81	2.72	1.81	2.75	1.84
Complex 2[a] (YEMCIC)	2.71	1.85	2.71	1.86	2.75	1.81
Complex 3[a]	2.68	1.81	2.68	1.78	2.67	1.79
HAJZOH[b]	2.64	1.80			2.66	1.79
XUWSEN[c]	2.75	1.83			3.16 2.73*	2.06 1.83*
QOSMOA[d]	2.70	1.81			2.83	1.87

a: ref. 1. ; b: ref. 5; c: ref. 3; d: ref. 4. *Structural parameters refer to the optimized structure of XUWSEN with no hydrogen atoms on the oxobridge oxygens.

TABLE S2: List of dMn compounds visualized in Figure 5. CSD codes, Mn-Mn, Mn-O distances and symbols employed in Figure 5 are also displayed.

CSD code	Mn-Mn distance [Å]	∑Mn-O (averaged over all four Mn-O distances) [Å]	“recognized” oxidation/protonation pattern	experimental oxidation/protonation pattern	symbol employed in Figure 5	References
EGILIQ	2.69	1.81	0H, IV-III	OH, IV-III	full circle	Inorg. Chem. 2008, 47 (18), 8306–8314
KIKUU	2.69	1.81	OH, IV-III	OH, IV, III	full circle	Chem. Commun. 2008, 383-385
MIKKOH	2.62	1.81	OH,IV-III	OH, IV-III	full circle	Polyhedron 2007, 26(15) 4557-4566
NAPYIN01	2.65	1.83	0H, IV-III	OH, III-III	empty circle	Eur. Chem. J. 2008, 14(10), 3013-3025
ZOPRUR	2.93	1.93	1H-2H, III-III	2H, III-III	Triangle	J. Coord. Chem. 2007, 60(10), 1083-1091
VEFTIK	2.95	2.06	2H-1H, III-II	2H, III-III	Triangle	Eur. J. Chem. 2006, 12(7), 1950-1959
FLOHMN01	3.2	2.05	2H, III-II	2H, ?	empty circle	Aust. J. Chem. 1980, 33, 1659
KUSGEK	3.16	2.03	2H, III-II	2H, ?	empty circle	J. Am. Chem. Soc. 1992, 114, 8719
PEGGUD	3.17	2.04	2H, III-II	2H, ?	empty circle	Angew. Chem. 1993, 32, 706
PEGHAK	3.18	2.05	2H, III-II	2H, ?	empty circle	Angew. Chem. 1993, 32, 706

FIGURES

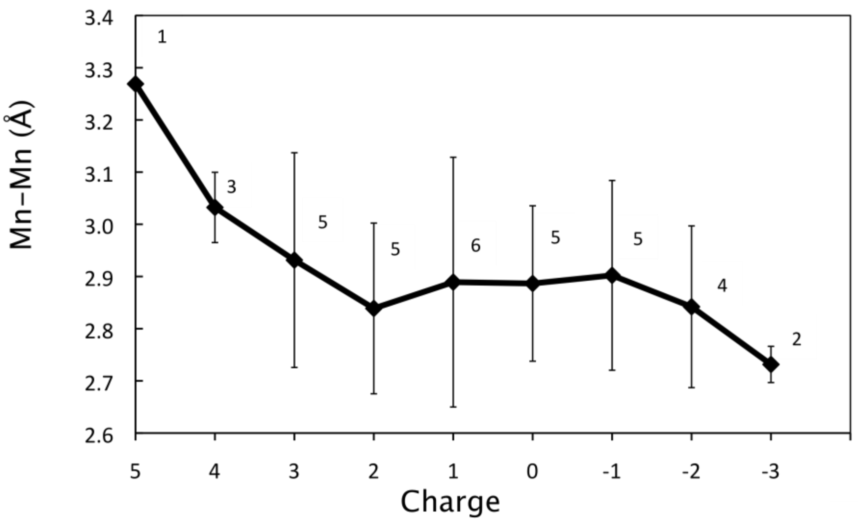

Figure S1. Mn-Mn distances as a function of the overall charge of the oxomanganese complexes. Squared data points are the average Mn-Mn distances of those complexes bearing the same charge. Numbers close to the data points indicate how many complexes have the same charge. Bars represent the standard deviation. Although the average Mn-Mn distances show a weak trend, complexes with the same charge have very different Mn-Mn distances, *i.e.*, the Mn-Mn distances are virtually independent of the overall charges of the compounds.

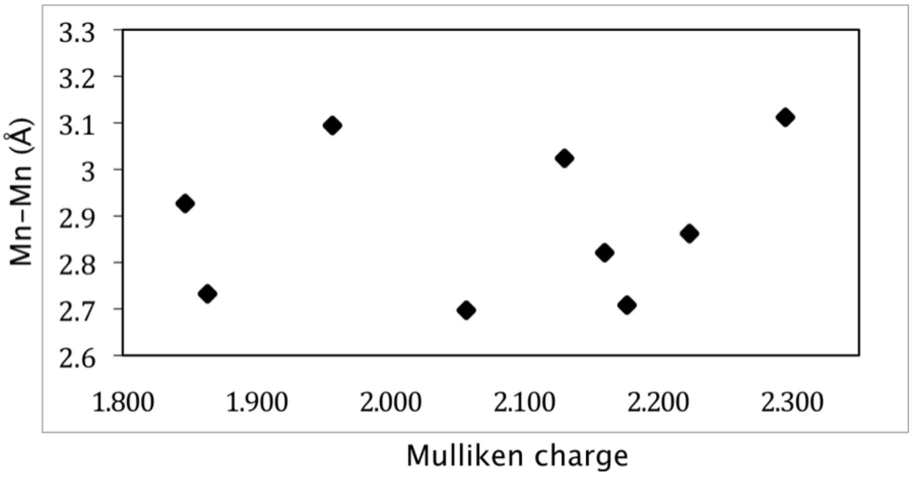

Figure S2. Mn-Mn distances (each data point averaged over four values belonging to the four dMn complexes) as a function of the sum of Mulliken charges on the manganese atoms.

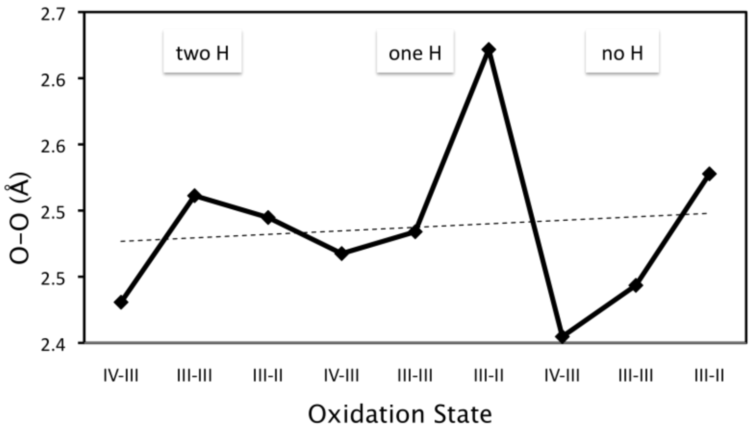

Figure S3: O-O distances as a function of the oxidation state and protonation state. TheO-O distance is virtually constant with the protonation state and does not show a clear trend with the oxidation state.

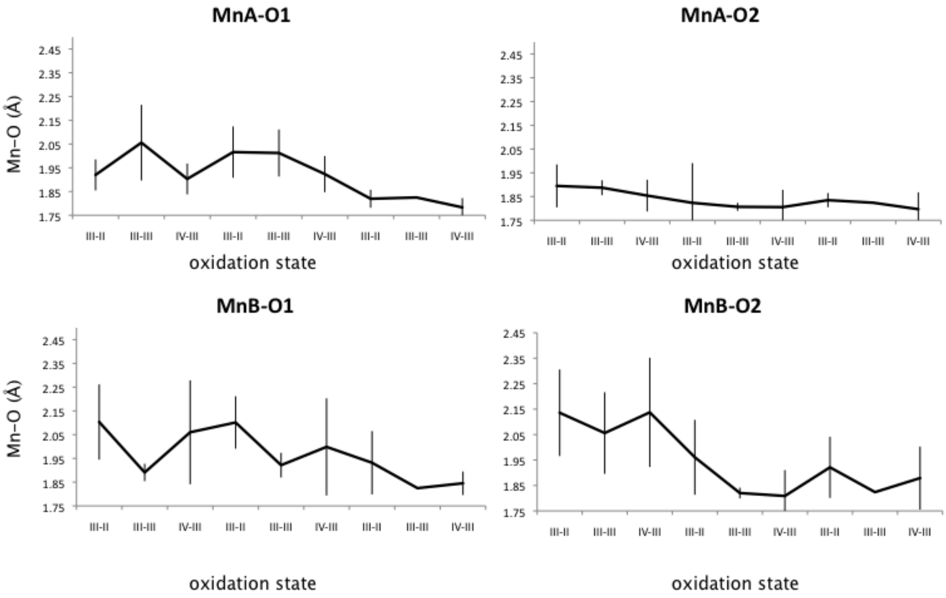

Figure S4. Mn-O distances as a function of the oxidation states and protonation pattern. Bars denote standard deviation. For nomenclature, see Figure 1b.

REFERENCES

1 Sproviero E. M., Gascon J. A., McEvoy J. P., Brudvig G. W. and Batista V. S., *J. Inorg. Biochem.*, 2006, **100**, 786.
2 Luber S., Rivalta I., Umena Y., Kawakami K., Shen J. R., Kamiya N., Brudvig G. W. and Batista V. S., *Biochemistry*, 2011, *in press*.
3 Si S. G., Tang J .K., Liao D. Z., Jiang Z. H. and Yan S. P., *J. Mol. Struct.*, 2002, **606**, 87.
4 Franceschi F., Guillemot G., Solari E., Floriani C., Re N., Birkedal H. and Pattison P., *Chem. Eur. J.*, 2001, **7**, 1468
5 Dave B. C., Czernusewicz, Bond M R. and Carrano C. J., *Inorg. Chem.*, 1993, **32**, 3593