Supporting information: Protonation and water exchange kinetics in sandwich polyoxometalates.

C. André Ohlin[1]

[1]Department of Chemistry, Umeå University, Sweden

Department of Chemistry, Umeå University, Sweden

Contents

List of Tables

List of Figures

Listings

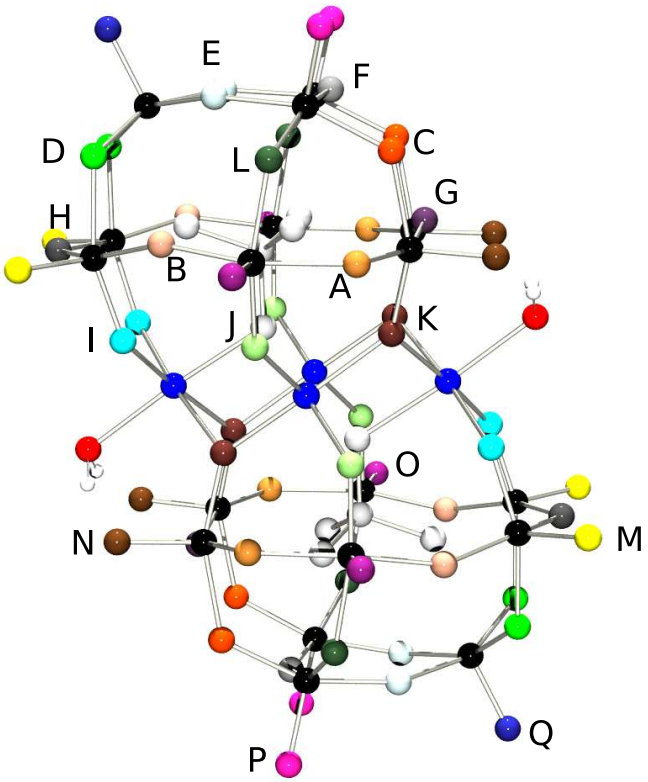

Figure S1: Structure of $[Zn_4(H_2O)_2(PW_9O_{34})_2]^{10-}$. μ_2-O sites are labelled A-J and L, the single μ_3-O site is labelled K, and the terminal η-O sites are labelled N-Q.

Table S1: Energies, bond distances and partial charges using different partition methods in $H_2[Zn_4(H_2O)_2(PW_9O_{34})_2]^{8-}$ as a function of protonation site. Geometries optimised at pbe0/def2-svp with PCM. The d(M−OH_2) in the non-protonated form is 2.192 Å. Partial charges were calculated for the unprotonated molecule.

Entry	Site	ϵ (Hartree)	$\Delta\epsilon$ (kcal/mol)	d(M−OH_2) (Å)	NBO[a] (a.u.)	MKUFF[b] (a.u.)	CHelpG[c] (a.u.)	HLYGAt[d] (a.u.)
1	A (μ_2)	-14271.4963027	23.026	2.171	-0.9212	-0.8996	-0.8946	-0.7597
2	B (μ_2)	-14271.5005239	20.378	2.166	-0.9379	-0.9492	-0.9098	-0.7476
3	C (μ_2)	-14271.5026127	19.067	2.167	-0.9279	-0.9000	-0.8750	-0.7821
4	D (μ_2)	-14271.5050184	17.557	2.169	-0.9355	-0.9091	-0.8667	-0.7774
5	E (μ_2)	-14271.5088241	15.169	2.168	-0.9404	-0.9243	-0.8716	-0.7510
6	F (μ_2)	-14271.5098391	14.532	2.162	-0.9381	-0.9236	-0.8859	-0.7524
7	G (μ_2)	-14271.5061181	16.867	2.164	-0.9325	-0.9560	-0.8883	-0.7946
8	H (μ_2)	-14271.5040763	18.148	2.171	-0.9344	-0.9112	-0.9134	-0.7677
9	I (μ_2)	-14271.5322401	0.476	2.156	-0.9581	-0.9626	-0.9230	-0.8581
10	J (μ_2)	-14271.5329979	0	2.160	-0.9614	-0.9553	-0.9477	-0.8166
11	K (μ_3)	-14271.5104687	14.137	2.167	*-1.0928*	*-1.0320*	*-1.0141*	*-1.0917*
12	L (μ_2)	-14271.4999138	20.760	2.162	-0.9422	-0.9318	-0.8967	-0.8009
13	M (η)	-14271.4608424	45.278	2.165	-0.7634	-0.7086	-0.7474	-0.6412
14	N (η)	-14271.4515435	51.113	2.167	-0.7908	-0.7139	-0.7506	-0.6506
15	O (η)	-14271.4604518	45.523	2.170	-0.7639	-0.7067	-0.7492	-0.6384
16	P (η)	-14271.4468487	54.059	2.175	-0.7537	-0.6858	-0.7261	-0.6226
17	Q (η)	-14271.4482246	53.196	2.172	-0.7561	-0.6903	-0.7211	-0.6281

[a] Natural atomic charges from Natural Bond Order analysis.[1] [b] The Mesler-Singh-Kollman scheme, using UFF radii.[2] [c] Breneman's modified CHelp scheme, using radii of 1.39 and 1.80 Å for Zn and W, respectively.[3] [d] The Hu, Lu, and Yang charge fitting method using G09 standard atom densities.[4] The most negatively charged oxygen for each method is given in italics.

Table S2: Energies and bond distances in $H_2[Zn_4(H_2O)_2(PW_9O_{34})_2]^{8-}$ (left) and $H_4[Zn_4(H_2O)_2(PW_9O_{34})_2]^{6-}$ (right) as a function of protonation site. Geometries optimised at pbe0/def-svp with PCM. The d(M−OH_2) in the non-protonated form is 2.192 Å.

		$(H_2[Zn_4(H_2O)_2(PW_9O_{34})_2]^{8-})$			*$(H_4[Zn_4(H_2O)_2(PW_9O_{34})_2]^{6-})$*		
Entry	Site	ϵ (Hartree)	$\Delta\epsilon$ (kcal/mol)	d(M−OH_2) (Å)	ϵ (Hartree)	$\Delta\epsilon$ (kcal/mol)	d(M−OH_2) (Å)
1	I	-14271.5322401	0.476	2.156	-14272.4578948	-0.294	2.119
2	J	-14271.5329979	0	2.160	-14272.4574264	0	2.132
3	K	-14271.5104687	14.137	2.167	-14272.4146286	26.856	2.130

$\Delta\epsilon$ given relative to the lowest energy configuration for each protonation state.

Table S3: Energies and bond distances in $H_2[Zn_4(H_2O)_2(PW_9O_{34})_2]^{8-}$ (left) and $H_4[Zn_4(H_2O)_2(PW_9O_{34})_2]^{6-}$ (right) as a function of protonation site. Geometries optimised at pbe0/def2-tzvp with PCM. The d(M−OH_2) in the non-protonated form is 2.236 Å.

		$(H_2[Zn_4(H_2O)_2(PW_9O_{34})_2]^{8-})$			$(H_4[Zn_4(H_2O)_2(PW_9O_{34})_2]^{6-})$		
Entry	Site	ϵ (Hartree)	$\Delta\epsilon$ (kcal/mol)	d(M−OH_2) (Å)	ϵ (Hartree)	$\Delta\epsilon$ (kcal/mol)	d(M−OH_2) (Å)
1	A (μ_2)	-14279.3302237	22.038	2.207	–	–	–
2	B (μ_2)	-14279.3322006	20.798	2.199	–	–	–
3	C (μ_2)	-14279.3341081	19.601	2.199	–	–	–
4	D (μ_2)	-14279.3372344	17.639	2.202	–	–	–
5	E (μ_2)	-14279.3383597	16.933	2.200	–	–	–
6	F (μ_2)	-14279.3391176	16.457	2.193	–	–	–
7	G (μ_2)	-14279.3357358	18.579	2.199	–	–	–
8	H (μ_2)	-14279.3386754	16.735	2.205	–	–	–
9	I (μ_2)	-14279.3653335	0.007	2.183	-14280.2894352	0.200	2.138
10	J (μ_2)	-14279.3653439	0	2.190	-14280.2897538	0	2.152
11	K (μ_3)	-14279.3439098	13.450	2.202	-14280.2457475	27.614	2.153
12	L (μ_2)	-14279.3321491	20.830	2.193	–	–	–
13	M (η)	-14279.3001521	40.908	2.197	–	–	–
14	N (η)	-14279.2907393	46.815	2.202	–	–	–
15	O (η)	-14279.2997023	41.190	2.202	–	–	–
16	P (η)	-14279.2845071	50.725	2.209	–	–	–
17	Q (η)	-14279.2861521	49.693	2.207	–	–	–

Table S4: Bond parameters obtained from crystal structures, and rates of aquo-ligand exchange. Average bond distances were used where there were several different types of water ligands.

Entry	Compound	M-O bond distance (Å)[a]	k (s^{-1}))	References
1	$[Ni(H_2O)_6]^{2+}$	2.030	$4.4 \cdot 10^4$	Structure,[5] and rate.[6]
2	$[Ni(H_2O)_6]^{2+}$	2.030	$3.2 \cdot 10^4$	Structure,[5] and rate.[7]
3	$[Ni(H_2O)_2(NCS)_4]^{2-}$	2.071	$1.1 \cdot 10^6$	Structure,[8] and rate.[9]
4	$[Ni(H_2O)_3(NH_3)_3]^{2+}$	2.085	$2.5 \cdot 10^5$	Structure,[10] and rate.[9]
5[b]	$[Ni(H_2O)_4(en)]^{2+}$	2.088	$4.4 \cdot 10^5$	Structure,[11] and rate.[6]
6	$[Ni(H_2O)_2(bipyridyl)_2]^{2+}$	2.090	$6.6 \cdot 10^4$	Structure,[12] and rate.[9]
7	$[Ni(H_2O)_5(NH_3)]^{2+}$	2.104	$1.6 \cdot 10^5$	Structure,[10] and rate.[13]

[a] Metal-to-oxygen distance. [b] en = ethylenediamine.

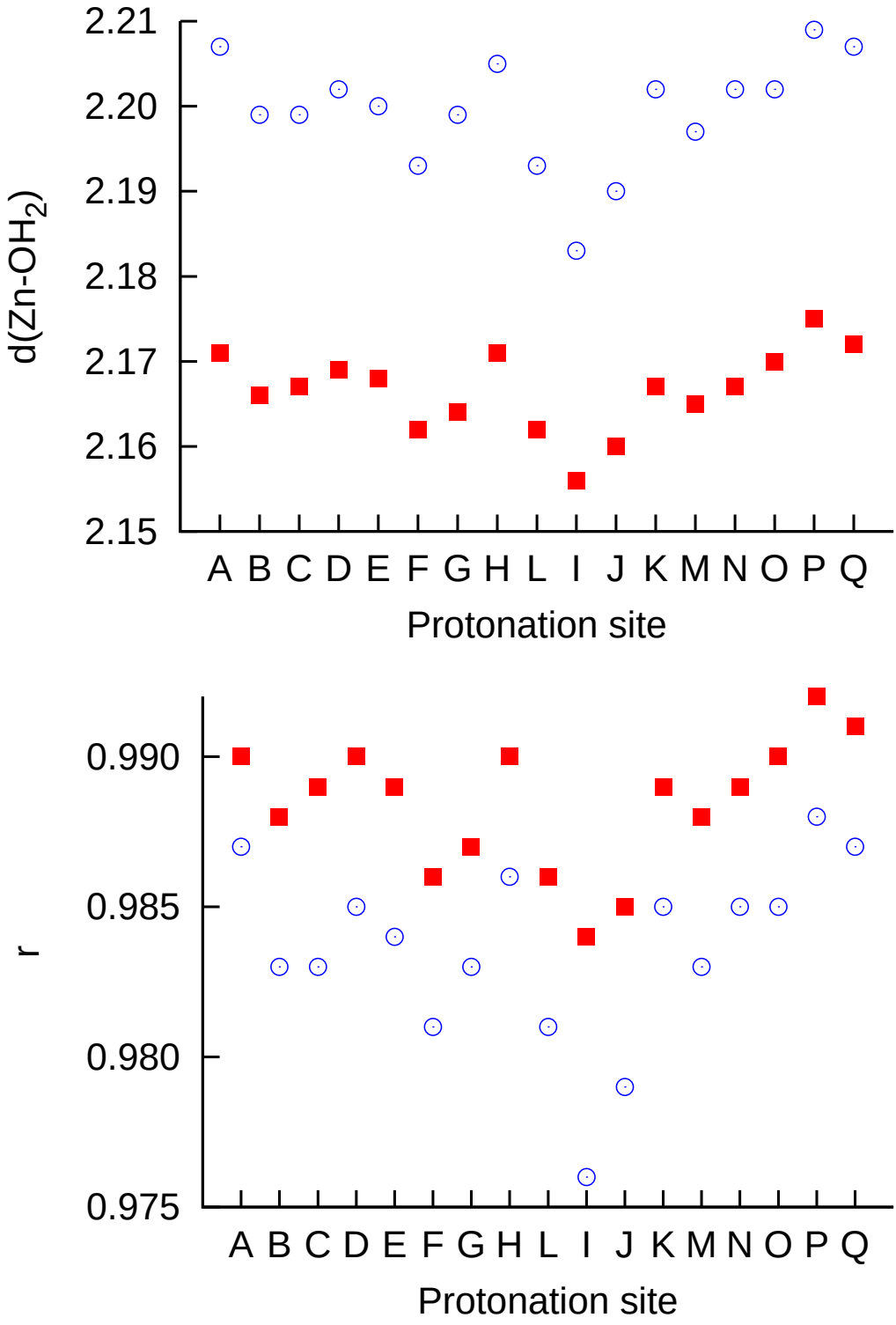

Figure S2: Top: Zn-OH_2 distance as a function of basis set. Bottom: r *vs* protonation site, where r is the Zn-OH_2 distance as a function of basis set divided by the Zn-OH_2 distance in the unprotonated complex at the same level of theory. Def2-svp results given as red squares and def2-tzvp data given as empty blue circles. The larger basis set gives longer absolute Zn$\overline{}$$OH_2$ distances, but also predicts a larger contraction due to protonation.

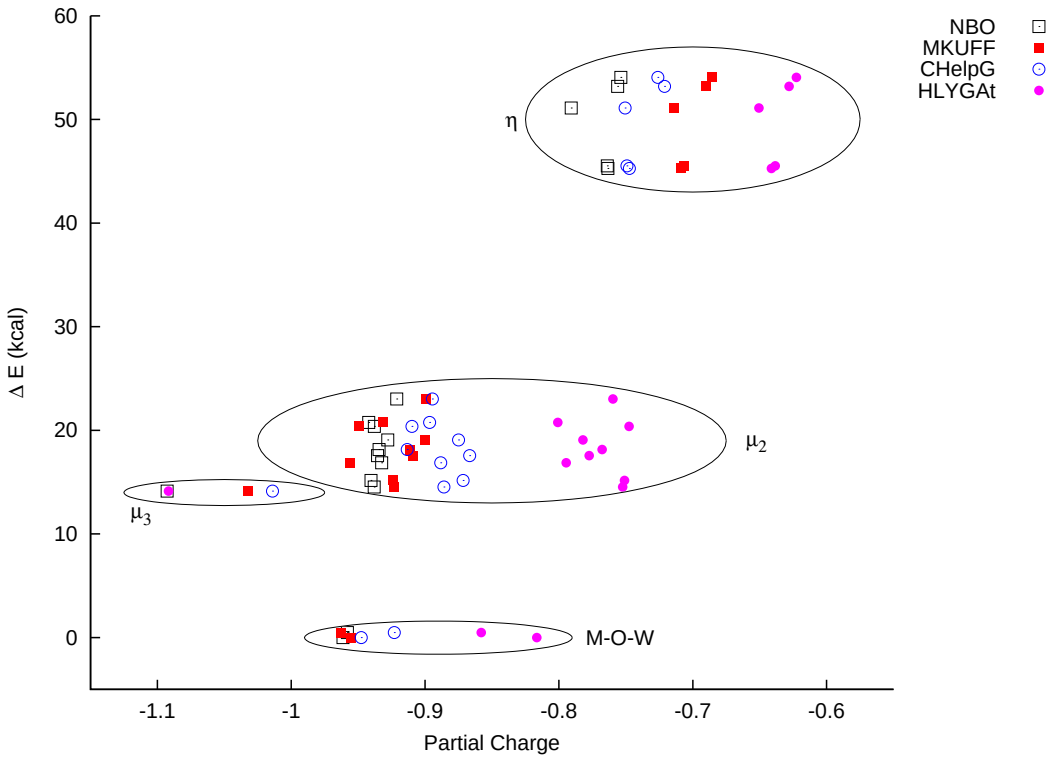

Figure S3: Comparison of partial charges from different methods at pbe0/def2-svp with relative energies of $H_2[Zn_4(H_2O)_2(PW_9O_{34})_2]^{8-}$ protonated in different loci. All partial charges methods indicate that site K (μ_3) has the most negative partial charge.

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