Supporting Information

Modeling of *M*Al_{12} Keggin Heteroatom Reactivity by Anion Adsorption

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S1. Structural Details

In this section are the coordinates for the DFT-optimized structures of the three heteroatom analogs. For a given analog, the final coordinates of the anions are also provided. Structural information for the Al_{13} analog can be found in: **DOI:** 10.1021/acs.inorgchem.7b01803, "Systematic Study of Aluminum Nanoclusters and Anion Adsorbates", Bennett *et al*., *Inorganic Chemistry*, **2017**, *56*, 21, 13014-13028.

S1.1 $GeAl_{12}$ Final Structure in XYZ Coordinates

Al	5.85580	9.96802	10.02812	O	7.94503	10.05274	10.03671
Al	5.85511	7.89987	7.99873	O	3.88941	10.04404	10.20728
Al	12.16211	7.99896	10.05638	O	8.09186	11.89115	11.79034
Al	12.15461	10.03148	7.98353	O	3.91511	7.66397	7.85118
Al	10.05145	5.83939	10.02837	O	8.10401	6.08489	6.08173
Al	8.02598	5.81704	7.94530	O	14.09188	7.77082	10.31845
Al	9.99369	12.13905	7.89599	O	9.88706	6.14487	11.86915
Al	7.92388	12.13324	9.93465	O	14.10251	10.22806	7.83217
Al	10.03963	9.97461	5.80940	O	9.94685	11.84585	6.03935
Al	7.97052	7.94813	5.84144	O	10.29408	3.90491	10.24027
Al	7.97534	10.06327	12.16391	O	11.88242	8.10586	11.90813
Al	10.02633	7.98181	12.18471	O	7.92008	3.85852	7.74618
Ge	9.00451	8.98029	8.99103	O	6.12350	8.03558	6.14771
O	12.15725	9.86189	9.84977	O	10.10445	14.07787	7.61974
O	12.28628	8.18406	8.21348	O	11.88286	9.87244	6.13501
O	5.92224	8.09865	9.86649	O	7.64021	14.07020	10.02840
O	5.75970	9.74578	8.18802	O	6.11989	9.90957	11.88355
O	9.75711	12.34723	9.71957	O	10.26883	10.14232	3.86582
O	8.11062	12.04616	8.05133	O	11.84988	11.88027	8.06162
O	9.88527	5.86439	8.14989	O	7.77745	7.83972	3.88334
O	8.21899	5.68939	9.78630	O	6.15609	6.04289	8.06853
O	9.82085	9.83309	12.28352	O	7.66931	10.43798	14.06500
O	8.18371	8.21994	12.31280	O	6.06550	11.83341	9.87752
O	8.18251	9.79923	5.78010	O	10.33083	7.66005	14.09921
O	9.82733	8.13074	5.75172	O	11.89792	6.13630	9.94747
O	7.94910	7.90820	7.93423	H	10.44242	12.36004	10.40203
O	10.06218	10.03610	7.92627	H	7.56508	12.64190	7.51180
O	10.05357	7.94170	10.07008	H	5.51084	12.37185	10.46716

H	7.68932	12.53130	12.40054
H	5.55791	10.47516	12.44044
H	12.43764	12.47938	7.57163
H	10.57574	12.36856	5.51348
H	12.49171	10.29319	5.50593
H	12.00473	7.51708	7.57098
H	12.60382	10.47584	10.45164
H	10.51916	10.50065	12.26108
H	7.48716	7.55178	12.26799
H	10.28041	5.51019	12.49076
H	12.42579	7.54049	12.48359
H	12.51018	5.59550	10.47415
H	10.49073	5.38232	7.56650
H	7.52303	5.66261	10.45638
H	5.44530	7.50286	10.46413
H	5.45254	10.39613	7.54072
H	5.49774	7.60411	5.54285
H	5.61752	5.47308	7.49340
H	7.50966	5.53072	5.54743
H	7.59122	10.44726	6.19185
H	10.44247	7.47839	5.38660
H	11.13826	3.47090	10.01183
H	9.58685	3.32048	9.90383
H	8.23543	3.39365	6.94743
H	7.16253	3.34454	8.08580
H	9.61030	7.29059	14.64476
H	10.77878	8.33250	14.64741
H	7.21790	9.77922	14.62671
H	8.38192	10.82652	14.60791
H	14.56574	8.26289	11.01582
H	14.66852	7.77892	9.53038
H	14.58646	11.02357	8.12385
H	14.60956	9.84525	7.09151
H	9.87133	9.43929	3.31495
H	10.04841	10.98417	3.42195
H	7.06419	8.33378	3.43491
H	7.90191	7.01251	3.37965
H	3.49275	6.80650	8.05172
H	3.34325	8.34844	8.25149
H	3.43441	9.72995	11.01259
H	3.37332	10.80644	9.88051
H	6.77212	14.49975	10.14654
H	8.29922	14.64666	10.45940
H	10.55180	14.64131	8.27921
H	10.22158	14.51266	6.75402

$GeAl_{12}$ Anion XYZ Coordinates

$GeAl_{12}$-Cl^-

Cl	8.14668	8.15808	16.02452

$GeAl_{12}$-NO_3^-

N	8.27683	8.16830	16.79717
O	7.47632	8.88780	17.41363
O	9.09544	7.40694	17.33578
O	8.24680	8.20099	15.47171

$GeAl_{12}$-SeO_4^{2-}

Se	8.09241	7.90117	16.42993
O	6.68042	8.53133	15.64266
O	7.74601	7.59861	18.03260
O	9.34307	9.03854	16.19149
O	8.54405	6.45283	15.61688

$GeAl_{12}$-SO_4^{2-}

S	7.88366	7.92232	16.60457
O	6.83012	8.41940	15.61254
O	7.24194	7.32760	17.79853
O	8.91555	8.96404	16.85253
O	8.61395	6.67101	15.88743

$GeAl_{12}$-PO_4^{3-}

P	8.14968	7.79477	16.74548
O	6.84987	8.51842	16.05907
O	7.72844	7.35569	18.13008
O	9.37740	8.68513	16.55551
O	8.37122	6.43023	15.84732

S1.2 $GaAl_{12}$ Final Structure in XYZ Coordinates

Al	5.91734	9.95849	10.02101
Al	5.92474	7.87011	7.98888
Al	12.10829	7.99928	10.06983
Al	12.10252	10.03414	7.97394
Al	10.06933	5.89238	10.04370
Al	8.04702	5.86108	7.93291
Al	10.00836	12.09437	7.88964
Al	7.91516	12.08022	9.93268
Al	10.04092	9.98920	5.86963
Al	7.97319	7.94996	5.90300
Al	7.96719	10.07160	12.11269
Al	10.03316	7.97781	12.14587
Ga	9.01564	8.97782	8.99509
O	12.14017	9.87547	9.85615
O	12.24221	8.17269	8.20945
O	5.96114	8.06926	9.87755
O	5.82447	9.73108	8.17079
O	9.76056	12.32288	9.72205
O	8.10972	12.03193	8.03544
O	9.91930	5.88381	8.14697
O	8.22876	5.70082	9.78249
O	9.82134	9.83954	12.29155
O	8.17918	8.22147	12.31923
O	8.16384	9.81855	5.83759
O	9.83303	8.13610	5.78160
O	7.91446	7.84616	7.88938
O	10.11556	10.09397	7.87928
O	10.10902	7.89500	10.13313
O	7.90300	10.09415	10.09057
O	3.90314	9.97537	10.12947
O	8.07187	11.92298	11.80881
O	3.94794	7.69440	7.90344
O	8.12121	6.06117	6.04849
O	14.07665	7.80526	10.28162
O	9.89377	6.11787	11.90398
O	14.08780	10.17715	7.85095
O	9.95973	11.87742	6.00932
O	10.25491	3.91680	10.19969
O	11.91247	8.11178	11.94277
O	8.00330	3.86023	7.77756
O	6.10118	8.00574	6.11680
O	10.08573	14.06377	7.64434
O	11.90821	9.87958	6.09992
O	7.64945	14.04792	9.98406
O	6.08667	9.91049	11.89531
O	10.18132	10.08449	3.88489
O	11.88695	11.91006	8.05589
O	7.83203	7.91516	3.89698
O	6.15277	5.99162	8.05949
O	7.66713	10.43217	14.04876
O	6.03106	11.84199	9.86198
O	10.31888	7.67746	14.09700
O	11.93494	6.11212	9.97236
H	10.44470	12.21539	10.39657
H	7.58742	12.66941	7.52191
H	5.48978	12.36531	10.47542
H	7.64867	12.55298	12.41320
H	5.53472	10.49712	12.43813
H	12.46526	12.49825	7.54444
H	10.62112	12.37278	5.49877
H	12.50758	10.32203	5.47872
H	11.81870	7.53407	7.61558
H	12.64023	10.47205	10.43238
H	10.52288	10.49552	12.18924
H	7.48059	7.56739	12.18840
H	10.29214	5.48819	12.52506
H	12.44380	7.52509	12.50613
H	12.52925	5.59094	10.53573
H	10.51273	5.35957	7.58852
H	7.52414	5.84186	10.42811
H	5.38854	7.51990	10.43487
H	5.45602	10.36093	7.53567
H	5.49289	7.53791	5.52353
H	5.62027	5.43556	7.46752
H	7.50837	5.51862	5.52546
H	7.64511	10.40531	6.41447
H	10.44593	7.48766	5.40789
H	11.09234	3.49282	9.93236
H	9.54810	3.42348	9.73669
H	8.28885	3.41504	6.95682
H	7.21877	3.37197	8.09316
H	9.55644	7.35838	14.61629
H	10.71886	8.39989	14.61775
H	7.26710	9.72125	14.58528
H	8.42252	10.77093	14.56619
H	14.53254	8.33120	10.96564
H	14.60336	7.90744	9.46540
H	14.56115	10.99028	8.10886
H	14.55666	9.82002	7.07336
H	9.64565	9.38826	3.45067
H	9.91804	10.91931	3.45180
H	7.07422	8.37891	3.49081

H	7.93380	7.07969	3.4014
H	3.52846	6.85056	8.15968
H	3.46901	8.38830	8.40216
H	3.45399	9.70873	10.95508
H	3.41765	10.75819	9.80330
H	6.78503	14.46411	10.15867
H	8.31846	14.59904	10.43174
H	10.55971	14.59656	8.31027
H	10.25202	14.48635	6.78119

$GaAl_{12}$-Cl^-

Cl	8.09233	8.12910	15.98794

$GaAl_{12}$-NO_3^-

N	8.29224	8.11962	16.76840
O	7.46770	8.78294	17.41950
O	9.17493	7.41013	17.28231
O	8.22187	8.15927	15.44885

$GaAl_{12}$-SeO_4^{2-}

Se	8.06965	7.88898	16.35432
O	6.62290	8.41269	15.58975
O	7.83280	7.67469	17.99462
O	9.27443	9.07918	16.02825
O	8.57872	6.42745	15.61314

$GaAl_{12}$-SO_4^{2-}

S	7.76928	7.65244	16.17573
O	6.67811	8.31221	15.28864
O	7.11284	6.99755	17.34282
O	8.78581	8.69598	16.54268
O	8.45530	6.56179	15.30941

$GaAl_{12}$-PO_4^{3-}

P	7.98877	7.83637	16.47017
O	6.63281	8.32281	15.69445
O	7.59300	7.40314	17.86469
O	9.06058	8.92020	16.28528
O	8.46987	6.49907	15.65239

S2. Mulliken Charge Analysis

Change in Mulliken Charge (Δq_m) in e			
Anion	$GaAl_{12}$	Al_{13}	$GeAl_{12}$
Cl^-	0.24	0.21	0.26
NO_3^-	0.20	0.16	0.22
SeO_4^{2-}	0.34	0.35	0.42
SO_4^{2-}	0.40	0.39	0.66
PO_4^{3-}	1.19	1.23	1.24

S3. Explicit Water Comparison

In the manuscript we employ implicit solvent (COSMO) to probe trends in Keggin adsorption reactivity using a set of test adsorbates that are present in the environment, during synthesis conditions, and ultimately found in isolable crystal structures. The implicit solvent model can be thought of as providing a screening charge limit, and we use this to delineate trends in adsorption reactivity that we can relate back to measurable properties and/or changes in the chemical environment. To connect better to experiment we can add explicit water to our DFT simulations and compare how the addition of explicit water will affect the properties presented in the manuscript. Here, we test how shielding by explicit water molecules influences electron sharing and the resulting structure, with a specific focus on the μ_4O-Al_o bond elongation to form a metastable intermediate.

A geometry optimization calculation, using the methods described in the manuscript, was performed on the Al_{13} Keggin interacting with a SO_4^{2-} anion, where four explicit water molecules are surrounding the anion. The water molecules were initialized at equivalent distances relative to the anion, approximately 3 Å from the oxyanion. After structural optimization, three water molecules rotated closer to SO_4^{2-}, where one of the hydrogen atoms partakes in a hydrogen-bond with the oxygen atoms of the anion, with distances of 1.8 Å. The fourth water molecule retains its distance of 3 Å.

Table S3: The following table compares differences between optimization that include either four or zero explicit water molecules interacting with a SO_4-Al_{13} Keggin complex.

No Explicit Water		4 Explicit Waters	
q_m (SO_4^{2-})	-1.609	q_m (SO_4^{2-})	-1.529
Δq_m (SO_4^{2-})	0.391	Δq_m (SO_4^{2-})	0.471
μ_4O-Al_o	A: 2.10 Å B: 2.14 Å	μ_4O-Al_o	A: 2.09 Å B: 2.12 Å

Comparing the Mulliken charge (q_m) on the SO_4^{2-} , shown in Table S2, we find that it is larger in magnitude without the presence of explicit water. When the four explicit water molecules are added to the calculation, this value becomes less negative, differing by 0.08 e between the two calculations. The water molecules seem to "soften" or shield the interaction of the Keggin and the SO_4^{2-} by taking on some of the excess charge. The water molecules should be neutral overall, but the residual Mulliken charge on the four water molecules ranges from -0.014 to -0.039 e. The same trends can be drawn by discussing the Δq_m values.

The elongation of the μ_4O-Al_o bonds is slightly impacted by the presence of water molecules, where the elongation of the two sides is smaller by 0.01-0.02 Å with water. The elongation is longer without water,

which is likely correlated to the more negative Mulliken charge causing a stronger effect on the structure. These test calculations show that inclusion of explicit water does screen more charge than implicit solvent alone, however the trends in geometry and adsorption induced electronic changes will remain the same as those presented in the manuscript.