Polyoxometalates with Internal Cavities: Redox Activity, Basicity and Cation Encapsulation in $[X^{n+}P_5W_{30}O_{110}]^{(15-n)-}$ Preyssler Complexes, with X = Na^+, Ca^{2+}, Y^{3+}, La^{3+}, Ce^{3+} and Th^{4+}

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Supplementary Information

Table S1. Optimized cartesian coordinates computed for $NaP_5W_{30}O_{110}^{14-}$ with a TZP-quality basis set and solvent effects (C_{5v} symmetry).

Total Binding Energy (COSMO) = –1244.2672 eV

Na	0.000000	0.000000	0.923345
P	-3.613502	0.000000	-0.010804
W	-3.257482	0.000000	3.473292
W	-5.974330	-1.923249	1.712075
W	-5.974330	1.923249	1.712075
O	-2.716224	0.000000	1.268328
O	-4.563388	-1.306522	0.007110
O	-4.563388	1.306522	0.007110
O	-6.477772	0.000000	1.628577
O	-4.590147	1.337550	2.903964
O	-4.590147	-1.337550	2.903964
O	-6.893139	-2.274018	0.007724
O	-6.893139	2.274018	0.007724
O	-1.927234	-1.400218	3.602842
O	-5.052202	-3.670639	1.616002
O	-3.759228	0.000000	5.175759
O	-7.296429	-2.416646	2.813015
O	-7.296429	2.416646	2.813015
P	-1.116634	-3.436645	-0.010804
W	-1.006617	-3.098049	3.473292
W	-0.017051	-6.276242	1.712075
W	-3.675288	-5.087608	1.712075
O	-0.839360	-2.583283	1.268328
O	-0.167588	-4.743777	0.007110
O	-2.652740	-3.936302	0.007110
O	-2.001742	-6.160727	1.628577
O	-2.690519	-3.952163	2.903964
O	-0.146347	-4.778815	2.903964
O	0.032622	-7.258475	0.007724
O	-4.292817	-5.853055	0.007724
O	0.736138	-2.265600	3.602842
O	1.929769	-5.939219	1.616002
O	-1.161665	-3.575238	5.175759
O	0.043646	-7.686101	2.813015
O	-4.553087	-6.192531	2.813015
P	2.923385	-2.123963	-0.010804
W	2.635358	-1.914700	3.473292
W	5.963792	-1.955682	1.712075
W	3.702877	-5.067564	1.712075
O	2.197472	-1.596557	1.268328
O	4.459812	-1.625294	0.007110
O	2.923904	-3.739290	0.007110
O	5.240628	-3.807539	1.628577
O	2.927315	-3.780122	2.903964
O	4.499699	-1.615920	2.903964
O	6.913301	-2.211967	0.007724
O	4.240033	-5.891405	0.007724
O	2.382193	0.000000	3.602842
O	6.244865	0.000000	1.616002
O	3.041280	-2.209619	5.175759
O	7.323404	-2.333626	2.813015
O	4.482466	-6.243841	2.813015
P	2.923385	2.123963	-0.010804
W	2.635358	1.914700	3.473292
W	3.702877	5.067564	1.712075
W	5.963792	1.955682	1.712075
O	2.197472	1.596557	1.268328
O	2.923904	3.739290	0.007110
O	4.459812	1.625294	0.007110
O	5.240628	3.807539	1.628577
O	4.499699	1.615920	2.903964
O	2.927315	3.780122	2.903964
O	4.240033	5.891405	0.007724

O	6.913301	2.211967	0.007724
O	0.736138	2.265600	3.602842
O	1.929769	5.939219	1.616002
O	3.041280	2.209619	5.175759
O	4.482466	6.243841	2.813015
O	7.323404	2.333626	2.813015
P	-1.116634	3.436645	-0.010804
W	-1.006617	3.098049	3.473292
W	-3.675288	5.087608	1.712075
W	-0.017051	6.276242	1.712075
O	-0.839360	2.583283	1.268328
O	-2.652740	3.936302	0.007110
O	-0.167588	4.743777	0.007110
O	-2.001742	6.160727	1.628577
O	-0.146347	4.778815	2.903964
O	-2.690519	3.952163	2.903964
O	-4.292817	5.853055	0.007724
O	0.032622	7.258475	0.007724
O	-1.927234	1.400218	3.602842
O	-5.052202	3.670639	1.616002
O	-1.161665	3.575238	5.175759
O	-4.553087	6.192531	2.813015
O	0.043646	7.686101	2.813015
W	-3.252722	0.000000	-3.470072
W	-5.976163	1.924181	-1.712702
W	-5.976163	-1.924181	-1.712702
O	-2.773610	0.000000	-1.313622
O	-6.479350	0.000000	-1.618577
O	-4.608265	-1.346885	-2.909740
O	-4.608265	1.346885	-2.909740
O	-1.936609	1.407029	-3.614413
O	-5.057319	3.674358	-1.610119
O	-3.782524	0.000000	-5.167041
O	-7.311310	2.420907	-2.795763
O	-7.311310	-2.420907	-2.795763
W	-1.005146	3.093522	-3.470072
W	-0.016731	6.278274	-1.712702
W	-3.676741	5.089065	-1.712702
O	-0.857093	2.637860	-1.313622
O	-2.002229	6.162228	-1.618577
O	-2.704996	3.966510	-2.909740
O	-0.143068	4.798930	-2.909740
O	0.739719	2.276621	-3.614413
O	1.931724	5.945236	-1.610119
O	-1.168864	3.597395	-5.167041
O	0.043101	7.701570	-2.795763
O	-4.561738	6.205367	-2.795763
W	2.631507	1.911902	-3.470072
W	5.965823	1.956006	-1.712702
W	3.703813	5.069396	-1.712702
O	2.243897	1.630287	-1.313622
O	5.241905	3.808467	-1.618577
O	2.936485	3.798323	-2.909740
O	4.519844	1.619017	-2.909740
O	2.393781	0.000000	-3.614413
O	6.251191	0.000000	-1.610119
O	3.060127	2.223312	-5.167041
O	7.337947	2.338925	-2.795763
O	4.492000	6.256035	-2.795763
W	2.631507	-1.911902	-3.470072
W	3.703813	-5.069396	-1.712702
W	5.965823	-1.956006	-1.712702
O	2.243897	-1.630287	-1.313622
O	5.241905	-3.808467	-1.618577
O	4.519844	-1.619017	-2.909740
O	2.936485	-3.798323	-2.909740
O	0.739719	-2.276621	-3.614413
O	1.931724	-5.945236	-1.610119

O	3.060127	-2.223312	-5.167041
O	4.492000	-6.256035	-2.795763
O	7.337947	-2.338925	-2.795763
W	-1.005146	-3.093522	-3.470072
W	-3.676741	-5.089065	-1.712702
W	-0.016731	-6.278274	-1.712702
O	-0.857093	-2.637860	-1.313622
O	-2.002229	-6.162228	-1.618577
O	-0.143068	-4.798930	-2.909740
O	-2.704996	-3.966510	-2.909740
O	-1.936609	-1.407029	-3.614413
O	-5.057319	-3.674358	-1.610119
O	-1.168864	-3.597395	-5.167041
O	-4.561738	-6.205367	-2.795763
O	0.043101	-7.701570	-2.795763

Table S2. Optimized cartesian coordinates computed for $Ce^{IV}(W_5O_{18})_2^{8-}$ with a TZP-quality basis set and solvent effects (C_{4v} symmetry).

Total Binding Energy (COSMO) = –431.3347 eV

O	0.000000	0.000000	-3.542345
W	0.000000	-2.325372	-3.306360
W	2.325372	0.000000	-3.306360
W	0.000000	2.325372	-3.306360
W	-2.325372	0.000000	-3.306360
Ce	0.000000	0.000000	0.000000
W	0.000000	0.000000	-5.787983
O	1.910123	-1.910123	-3.430099
O	1.910123	1.910123	-3.430099
O	-1.910123	1.910123	-3.430099
O	-1.910123	-1.910123	-3.430099
O	1.969870	0.000000	-1.509407
O	-1.969870	0.000000	-1.509407
O	-1.888780	0.000000	-5.327014
O	1.888780	0.000000	-5.327014
O	0.000000	1.969870	-1.509407
O	0.000000	-1.969870	-1.509407
O	0.000000	-1.888780	-5.327014
O	0.000000	1.888780	-5.327014
O	0.000000	-4.103821	-3.463072
O	0.000000	4.103821	-3.463072
O	0.000000	0.000000	-7.604637
O	4.103821	0.000000	-3.463072
O	-4.103821	0.000000	-3.463072
O	0.000000	0.000000	3.542345
W	0.000000	-2.325372	3.306360
W	2.325372	0.000000	3.306360
W	0.000000	2.325372	3.306360
W	-2.325372	0.000000	3.306360
W	0.000000	0.000000	5.787983
O	1.910123	-1.910123	3.430099
O	1.910123	1.910123	3.430099
O	-1.910123	1.910123	3.430099
O	-1.910123	-1.910123	3.430099
O	1.969870	0.000000	1.509407
O	-1.969870	0.000000	1.509407
O	-1.888780	0.000000	5.327014
O	1.888780	0.000000	5.327014
O	0.000000	1.969870	1.509407
O	0.000000	-1.969870	1.509407
O	0.000000	-1.888780	5.327014
O	0.000000	1.888780	5.327014
O	0.000000	-4.103821	3.463072
O	0.000000	4.103821	3.463072

O	0.000000	0.000000	7.604637
O	4.103821	0.000000	3.463072
O	-4.103821	0.000000	3.463072

Table S3. Cartesian coordinates computed for the protonated $NaHP_5W_{30}O_{110}^{14-}$ optimized in gas phase with a TZP-quality basis set. The energy corresponds to a single point calculation with the solvent effects (no symmetry).

Total Binding Energy (COSMO) = –1245.1290 eV

Na	0.218070	1.197286	0.000000
P	-3.587142	0.097042	0.000000
W	-3.260848	3.562425	0.000000
W	-5.955634	1.731452	1.927088
W	-5.955634	1.731452	-1.927088
O	-2.613852	1.265904	0.000000
O	-4.456754	-0.009540	1.290598
O	-4.456754	-0.009540	-1.290598
O	-6.420376	1.604447	0.000000
O	-4.555306	2.914565	-1.327686
O	-4.555306	2.914565	1.327686
O	-6.836874	0.000128	2.251411
O	-6.836874	0.000128	-2.251411
O	-1.920146	3.642097	1.383678
O	-5.059486	1.637163	3.649442
O	-3.776836	5.255725	0.000000
O	-7.285041	2.825055	2.382541
O	-7.285041	2.825055	-2.382541
P	-1.119923	-0.010926	3.393228
W	-1.004652	3.495187	3.092160
W	0.001486	1.700052	6.252340
W	-3.651069	1.710523	5.074618
O	-0.830142	1.254757	2.558071
O	-0.184607	-0.019612	4.687071
O	-2.630842	0.010079	3.906561
O	-2.005136	1.626904	6.129867
O	-2.696079	2.899406	3.908857
O	-0.146753	2.879923	4.745832
O	0.025191	-0.002276	7.220826
O	-4.315645	-0.000892	5.799424
O	0.726047	3.606599	2.234840
O	1.922639	1.634501	5.935884
O	-1.151607	5.188838	3.589403
O	0.022360	2.803263	7.654715
O	-4.531915	2.815717	6.164545
P	2.912520	0.002911	2.115585
W	2.641702	3.497759	1.916848
W	5.961614	1.716998	1.949495
W	3.707753	1.716353	5.050802
O	2.199893	1.268610	1.589219
O	4.432578	0.015148	1.631011
O	2.925752	0.024121	3.710583
O	5.230524	1.643815	3.805713
O	2.915534	2.918813	3.773567
O	4.494299	2.918488	1.615999
O	6.901771	0.011222	2.201869
O	4.218656	0.015044	5.891987
O	2.366316	3.602546	0.000000
O	6.241487	1.636537	0.000000
O	3.032371	5.200934	2.212881
O	7.310703	2.819874	2.332254
O	4.477395	2.816715	6.225710
P	2.912520	0.002911	-2.115585
W	2.641702	3.497759	-1.916848

W	3.707753	1.716353	-5.050802
W	5.961614	1.716998	-1.949495
O	2.199893	1.268610	-1.589219
O	2.925752	0.024121	-3.710583
O	4.432578	0.015148	-1.631011
O	5.230524	1.643815	-3.805713
O	4.494299	2.918488	-1.615999
O	2.915534	2.918813	-3.773567
O	4.218656	0.015044	-5.891987
O	6.901771	0.011222	-2.201869
O	0.726047	3.606599	-2.234840
O	1.922639	1.634501	-5.935884
O	3.032371	5.200934	-2.212881
O	4.477395	2.816715	-6.225710
O	7.310703	2.819874	-2.332254
P	-1.119923	-0.010926	-3.393228
W	-1.004652	3.495187	-3.092160
W	-3.651069	1.710523	-5.074618
W	0.001486	1.700052	-6.252340
O	-0.830142	1.254757	-2.558071
O	-2.630842	0.010079	-3.906561
O	-0.184607	-0.019612	-4.687071
O	-2.005136	1.626904	-6.129867
O	-0.146753	2.879923	-4.745832
O	-2.696079	2.899406	-3.908857
O	-4.315645	-0.000892	-5.799424
O	0.025191	-0.002276	-7.220826
O	-1.920146	3.642097	-1.383678
O	-5.059486	1.637163	-3.649442
O	-1.151607	5.188838	-3.589403
O	-4.531915	2.815717	-6.164545
O	0.022360	2.803263	-7.654715
W	-3.345181	-3.686490	0.000000
W	-5.963548	-1.734698	-1.927426
W	-5.963548	-1.734698	1.927426
O	-2.712522	-1.296249	0.000000
O	-6.422457	-1.599266	0.000000
O	-4.604103	-2.987743	1.319144
O	-4.604103	-2.987743	-1.319144
O	-1.983674	-3.686025	-1.367833
O	-5.047737	-1.634534	-3.629400
O	-3.835302	-5.382676	0.000000
O	-7.301177	-2.811947	-2.402719
O	-7.301177	-2.811947	2.402719
W	-1.034096	-3.485128	-3.062485
W	-0.004718	-1.720466	-6.235223
W	-3.657881	-1.714966	-5.087453
O	-0.905354	-1.308540	-2.577596
O	-2.018819	-1.621975	-6.135464
O	-2.716705	-2.933536	-3.951554
O	-0.161529	-2.909490	-4.754738
O	0.705012	-3.595991	-2.246971
O	1.921237	-1.611750	-5.923033
O	-1.167990	-5.179278	-3.571091
O	0.045042	-2.821490	-7.641207
O	-4.570241	-2.785837	-6.189474
W	2.609108	-3.453344	-1.909123
W	5.947132	-1.707522	-1.946120
W	3.705882	-1.707034	-5.053376
O	2.237574	-1.292063	-1.634905
O	5.225306	-1.600788	-3.804456
O	2.919775	-2.904115	-3.788284
O	4.506060	-2.915338	-1.629109
O	2.374351	-3.581712	0.000000
O	6.235507	-1.607467	0.000000
O	3.015663	-5.155461	-2.215528
O	7.305505	-2.796275	-2.334430
O	4.482634	-2.802894	-6.229681

W	2.609108	-3.453344	1.909123
W	3.705882	-1.707034	5.053376
W	5.947132	-1.707522	1.946120
O	2.237574	-1.292063	1.634905
O	5.225306	-1.600788	3.804456
O	4.506060	-2.915338	1.629109
O	2.919775	-2.904115	3.788284
O	0.705012	-3.595991	2.246971
O	1.921237	-1.611750	5.923033
O	3.015663	-5.155461	2.215528
O	4.482634	-2.802894	6.229681
O	7.305505	-2.796275	2.334430
W	-1.034096	-3.485128	3.062485
W	-3.657881	-1.714966	5.087453
W	-0.004718	-1.720466	6.235223
O	-0.905354	-1.308540	2.577596
O	-2.018819	-1.621975	6.135464
O	-0.161529	-2.909490	4.754738
O	-2.716705	-2.933536	3.951554
O	-1.983674	-3.686025	1.367833
O	-5.047737	-1.634534	3.629400
O	-1.167990	-5.179278	3.571091
O	-4.570241	-2.785837	6.189474
O	0.045042	-2.821490	7.641207
H	-1.743949	-1.163022	0.000000

Table S4. Calculated absolute HOMO and LUMO energies and H-L gaps, in eV, for the $[XP_5W_{30}O_{110}]^{(15-n)-}$ and $[|XH_2O|P_5W_{30}O_{110}]^{(15-n)-}$ polyoxoanions. Computed in gas phase and with solvent.

	Symmetry	Vacuum	Solvent		
		H-L Gap	*E*(LUMO)	*E*(HOMO)	H-L Gap
$[NaPA]^{14-}$	D_{5h}	1.94	–3.85	–5.78	1.93
$[NaPA]^{14-}$	C_{5v}	1.93	–3.99	–5.84	1.86
$[|NaH_2O|PA]^{14-}$	C_s	0.99 (1.86)	–4.04	–5.04	1.00 (1.79)
$[CaPA]^{13-}$	C_{5v}	1.89	–4.08	–5.86	1.78
$[|CaH_2O|PA]^{13-}$	C_s	1.03 (1.85)	–4.11	–5.77	1.65 (1.82)
$[YPA]^{12-}$	C_{5v}	1.98	–4.02	–5.79	1.76
$[|YH_2O|PA]^{12-}$	C_s	1.94	–4.05	–5.94	1.89
$[ThPA]^{11-}$	C_{5v}	1.79	–4.33	–6.02	1.69
$[|ThH_2O|PA]^{11-}$	C_s	1.81	–4.87	–6.68	1.81

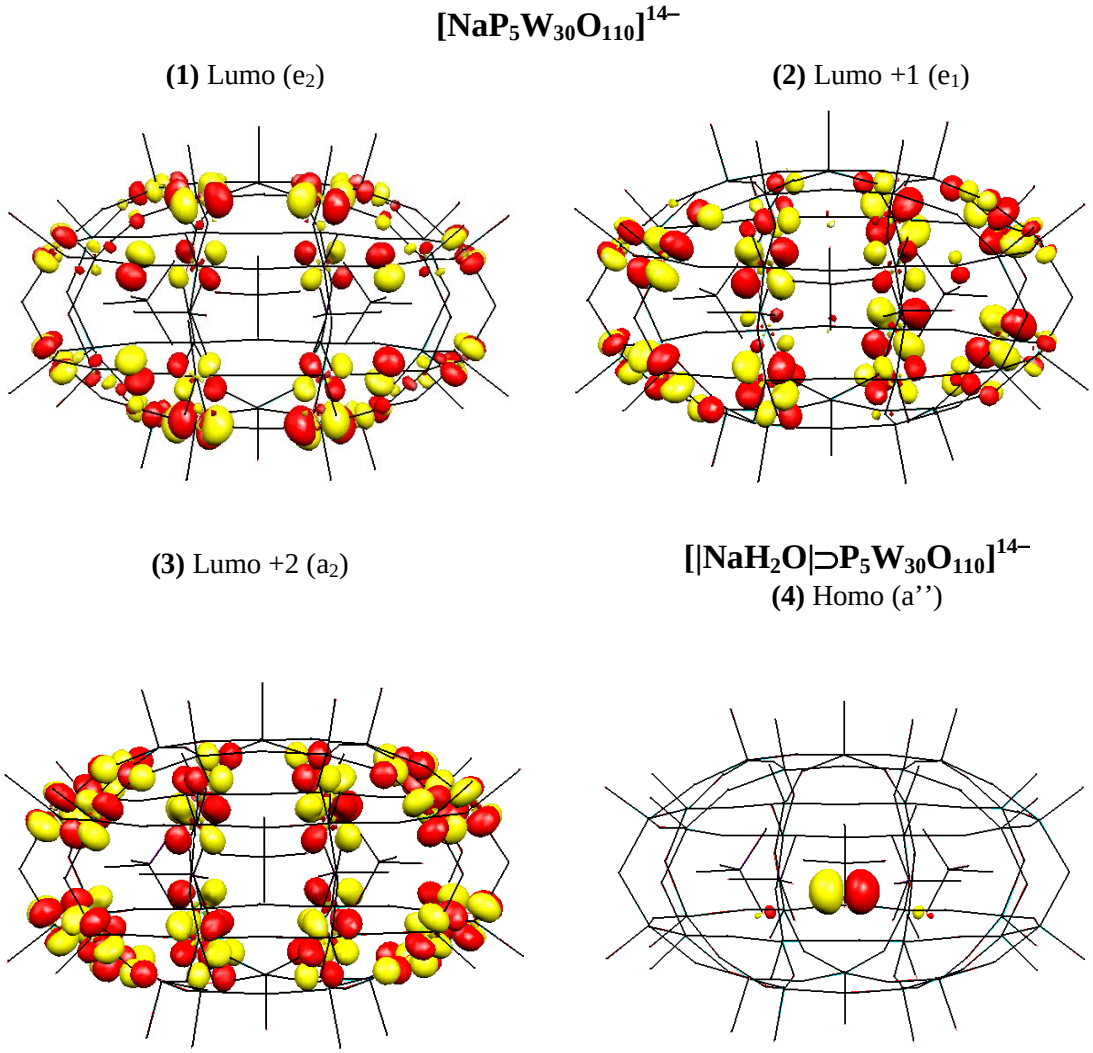


Figure S1. 3D representation of the LUMO, LUMO+1 and LUMO+2 of $[NaPA]^{14-}$, (1), (2) and (3) respectively; (4) shows the HOMO of $[|NaH_2O|\supset PA]^{14-}$, this orbital is a p_z-oxygen type coming from the water molecule.

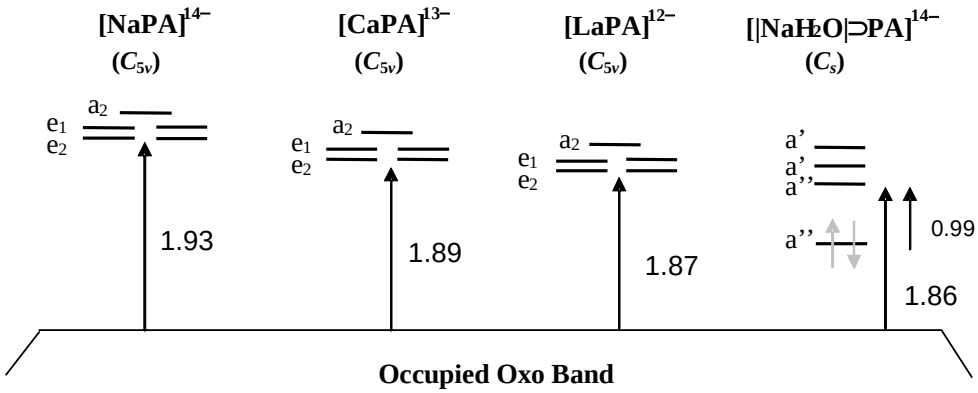
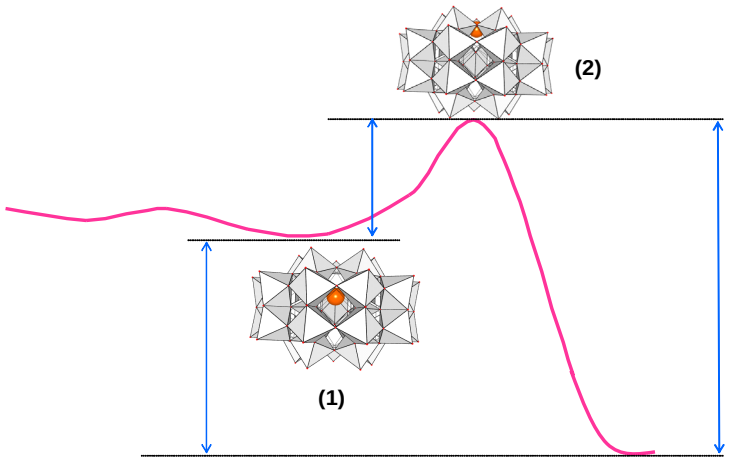


Figure S2. Molecular orbitals scheme for the $[X^{n+}PA]^{q-}$ anions and $[|NaH_2O|PA]^{14-}$. The water orbital is located between the occupied oxo-band and the unoccupied metal-band, reducing the HOMO-LUMO gap from 1.93 to 0.99 eV.

Fragment interaction energy analysis for X^{n+} and $P_5W_{30}O_{110}^{15-}$. The decomposition energy was carried out following the method developed by Ziegler et al. (Ziegler, T.; Rauk, A. *Theor. Chim. Acta* **1977**, *46*, 1; Ziegler, T.; Rauk, A. *Inorg. Chem.* **1979**, *18*, 1558).



	$NaP_5W_{30}O_{110}^{14-}$		$ThP_5W_{30}O_{110}^{11-}$	
	(1)	(2)	(1)	(2)
Pauli	0.54	1.38	11.20	17.04
Steric	–29.62	–27.76	–118.26	–111.80
Orbital	–2.06	–2.38	–40.26	–43.65
Total	–31.68	–30.15	–158.44	–155.46

Figure S3. Decomposition of the total interaction energy (in eV) for the $NaPA^{14-}$ and $ThPA^{11-}$ Preyssler-type polyoxoanions, (1) corresponding to the geometry in the minimum and (2) featuring the internal cation at the framework window. The deformation energy of the cage fragment between (1) and (2) is +1.31 and +4.60 eV for Na^+ and Th^{4+}.