Detailed Syntheses

$K_5H[Co^{II}W_{12}O_{40}]\bullet 15H_2O$ (1). The synthesis was adapted from published methods.[1] Sodium tungstate dihydrate (19.8 g, 60 mmol) was dissolved with stirring in 40 mL of deionized water. The pH was adjusted to 7.0 using glacial acetic acid. A solution of cobalt(II) acetate tetrahydrate was prepared (2.5 g, 10 mmol) by addition to 12 mL deionized water, with the pH adjusted to ~7 by the addition of a few drops of glacial acetic acid. Both solutions were heated with stirring until near boiling and the cobalt(II) acetate solution was added to the sodium tungstate solution slowly with stirring, yielding a dark green solution. The mixture was boiled for 20 minutes and filtered hot. A saturated solution of potassium acetate adjusted to pH 7.0 by the addition of glacial acetic acid was prepared while the filtrate was reheated. The potassium acetate solution was added slowly to the filtrate with stirring, precipitating a green solid. The resulting mixture was allowed to cool to room temperature and filtered, rinsing the solid twice with the filtrate. The solid was redissolved in 40 mL 2M H_2SO_4 with stirring and gentle heating for 15 minutes, yielding a dark blue solution. Insoluble material was removed by filtration. The solution volume was reduced by half through gentle heating, then allowed to develop crystals via slow evaporation. The dark blue crystals collected from the mother liquor were further purified by passing a concentrated solution through Dowex 50WX8 ion-exchange resin conditioned in the K^+ cycle to remove a large excess of latent cobalt cations. The eluent was evaporated to dryness using a rotary evaporator. The amorphous solid was dissolved in minimal 1M HCl and allowed to develop crystals of **1** via slow evaporation. FTIR (KBr pellet), $\tilde{\nu}$, cm^{-1}: 943 (s), 889 (s), 739 (s), 692 (sh), 580 (w), 449 (m). UV-vis (H_2O), λ_{max}, nm (ε, L mol^{-1} cm^{-1}): 625 (217).

$(C_{16}H_{36}N)_4H_2[Co^{II}W_{12}O_{40}]$ (1-TBA). From a 10.0 gram sample of **1** dissolved in minimal 2M H_2SO_4, the heteropoly acid, $H_6[Co^{II}W_{12}O_{40}]$ was prepared by the addition of concentrated H_2SO_4 and extraction with diethyl ether, using the etherate method.[2] Cation metathesis was accomplished by addition of a stoichiometric equivalent of $(C_{16}H_{36}N)Br$ dissolved in MeCN.[3] A solution of $(C_{16}H_{36}N)Br$ **(**2.17 g, 6.7 mmol) in 25 mL MeCN was added dropwise to a concentrated aqueous solution of the heteropoly acid with vigorous stirring, yielding the dark blue MeCN-soluble **1-TBA**. The solid was crashed out by addition of excess deionized water, then recovered by filtration. Repeated dissolution in MeCN and precipitation with water yielded pure **1-TBA** as a dark blue powder, which yields dark blue crystals by slow evaporation from MeCN. FTIR (KBr pellet), $\tilde{\nu}$, cm^{-1}: 3442 (w), 3200 (w), 2961 (s), 2935 (s), 2873 (s), 1630 (w), 1484 (s), 1381 (s), 945 (vs), 877 (vs), 759 (vs), 731 (sh), 688 (sh), 559 (w), 445 (m). UV-vis (H_2O), λ_{max}, nm (ε, L mol^{-1} cm^{-1}): 628 (205). Elemental analysis: calcd. (found) for $C_{64}H_{146}N_4Co_1W_{12}O_{40}$, %: C, 19.83 (20.06); H, 3.80 (3.89); N, 1.45 (1.56). TGA shows a mass loss of 26.3% between 300 and 420 °C (calcd. 25.1% for TBA_4H_2**1**).

$K_5[Co^{III}W_{12}O_{40}]\bullet 20H_2O$ (2). The synthesis was adapted from published methods.[1] Sodium tungstate dihydrate (19.8 g, 60 mmol) was dissolved with stirring in 40 mL of deionized water. The pH was adjusted to 7.0 using glacial acetic acid. A solution of cobalt(II) acetate tetrahydrate was prepared (2.5 g, 10 mmol) by addition to 12 mL deionized water, the pH being adjusted to ~7 by the addition of a few drops of glacial acetic acid. Both solutions were heated with stirring until near boiling and the cobalt(II) acetate solution was added to the sodium tungstate solution slowly with stirring, yielding a dark green solution. The mixture was boiled for 20 minutes and filtered hot. A saturated solution of potassium acetate adjusted to pH 7.0 by the addition of glacial acetic acid was prepared while the filtrate was reheated. The potassium acetate solution was added slowly to the filtrate with stirring, precipitating a

green solid. The resulting mixture was allowed to cool to room temperature and filtered, rinsing the solid twice with the filtrate. The solid was redissolved in 40 mL 2M H_2SO_4 with stirring and gentle heating for 15 minutes, yielding a dark blue solution. Insoluble material was removed by filtration. The filtrate was reheated to boiling and potassium persulfate (10 g, 37 mmol) was added in small portions until the color change from blue to yellow was complete. The solution was cooled in ice and the yellow needle crystals were collected by filtration. The product was further purified by passing a concentrated solution through Dowex 50WX8 ion-exchange resin conditioned in the K^+ cycle. The eluent was evaporated to dryness using a rotary evaporator. The yellow solid was dissolved in minimal deionized water, heated to boiling, and a small amount of potassium persulfate was added to ensure complete oxidation. Yellow needle crystals of **2** were obtained via slow evaporation and recrystallized twice from hot water. FTIR (KBr pellet), $\tilde{\nu}$, cm^{-1}: 954 (s), 896 (sh), 876 (s), 757 (vs), 498 (w), 440 (m). UV-vis (H_2O), λ_{max}, nm (ε, L mol^{-1} cm^{-1}): 389 (795).

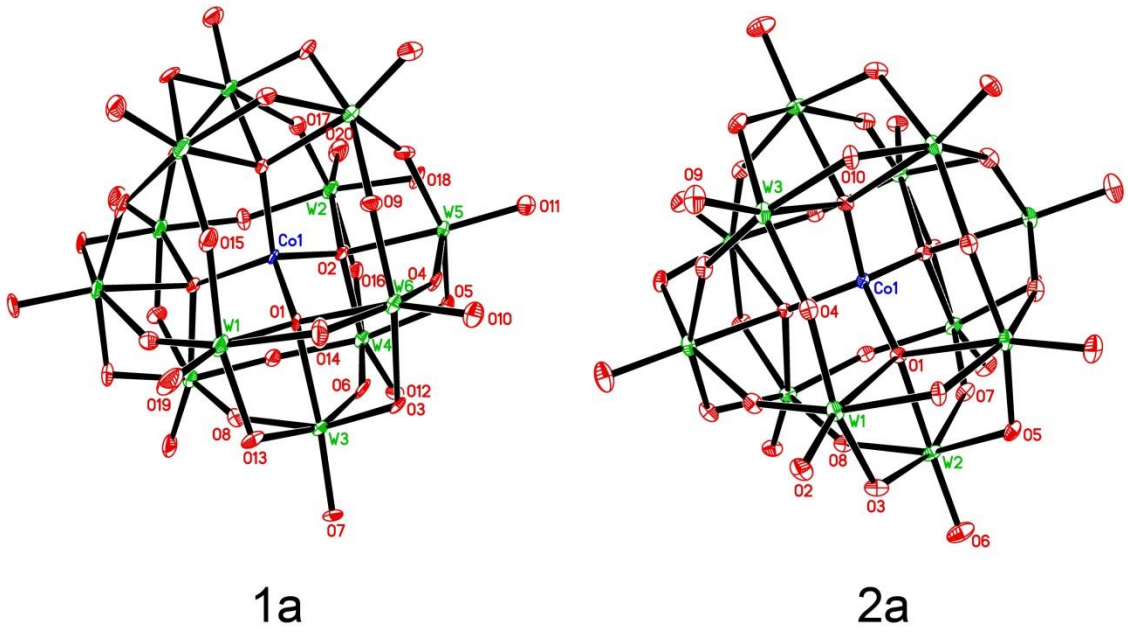

Figure S1. ORTEP representations of the cluster anions **1a** and **2a**, thermal ellipsoids are drawn at the 30% probability level. Color scheme: Co, blue; O, red; W, green.

Complete Citation for Reference 42:

M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. J. A. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. M. N.

Rega, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, V. G. Z. K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, J. B. F. Ö. Farkas, J. V. Ortiz, J. Cioslowski and D. J. Fox in *Gaussian 09, Vol.* (Ed. I. Gaussian), Wallingford CT., **2009**.

Table S1. Full calculated geometries (in Å) for all four anions at their different lower-lying electronic states.

Anion cluster 1a (quartet)

Atom	*X*	*Y*	*Z*
O	-4.697686	0.056001	-2.408827
O	-1.218916	3.23763	-3.98886
O	-0.773446	-1.617384	-4.96605
O	0.551	-0.758212	4.014741
O	2.474895	1.000287	3.1428
O	2.720043	-1.683626	2.601325
O	0.969729	-3.041488	0.966173
O	-1.069292	-2.171425	2.294869
O	-1.349081	0.901033	2.912564
O	0.459948	2.558118	2.093637
O	0.971481	-3.532714	3.80236
O	2.942403	1.498693	0.476042
O	3.172912	-1.026533	-0.033272
O	-1.375375	-3.035547	-0.124485
O	-3.424058	-0.749858	2.171602
O	-1.886019	2.559784	1.003652
O	1.565129	3.813807	-0.092699
O	2.637077	0.632911	-1.94266
O	2.20213	-3.148677	-1.493821
O	-3.749713	-1.669893	-0.397756
O	-3.994422	1.013722	0.142457
O	0.473536	1.912008	4.898529
O	-0.928333	3.817865	-1.250031
O	1.240435	2.893048	-2.663057
O	1.632272	-1.385166	-3.524012
O	-0.290733	-3.144417	-2.651913
O	-2.027465	-1.019105	-2.444696
O	-2.257081	1.506494	-1.935676
O	-0.217943	0.636863	-3.265135
O	0.966234	-0.241653	1.639449
O	-1.876832	-0.23713	0.322105
O	0.316412	1.769168	-0.673071

O	4.873758	0.036032	2.032176
O	0.59572	-1.29013	-1.289024
O	-3.541277	-3.523882	1.708699
O	-4.038466	1.922701	2.806224
O	-0.560515	5.105706	1.224638
O	3.841205	3.229629	-1.641521
O	4.286332	-1.627995	-2.61895
O	0.383733	-5.197311	-0.848404
Co	0.000489	-0.000061	-0.000049
W	-3.28321	-0.026975	-1.358283
W	-0.647742	2.383919	-2.554887
W	-0.312199	-1.294084	-3.294641
W	0.825134	-2.173067	2.688365
W	0.526964	1.082748	3.34273
W	3.158183	-0.03945	1.629538
W	-2.591704	-2.166673	1.102656
W	-2.890485	1.088776	1.758457
W	-0.254735	3.499766	0.562604
W	2.376623	2.378054	-1.150897
W	2.713053	-1.299321	-1.892403
W	0.379969	-3.4336	-0.833234

Anion cluster 2a (quintet)

Atom	*X*	*Y*	*Z*
O	3.733964	-0.06022	3.748996
O	0.233028	-3.57103	3.884204
O	3.734894	-3.73084	0.371293
O	-1.53115	3.377422	-1.67463
O	-3.46619	1.471825	-1.59961
O	-1.53164	1.387127	-3.50491
O	1.124597	0.996714	-2.98432
O	1.126568	2.893034	-1.24405
O	-1.12556	2.984163	0.996802
O	-2.9766	1.180597	1.087272
O	0.230594	3.571065	-3.88429
O	-2.97686	-1.18133	-1.08611
O	-1.12749	-1.24394	-2.89249
O	2.976338	1.086941	-1.18159
O	1.530772	3.505414	1.386956
O	-1.12658	1.24376	2.89298

O	-3.46526	-1.47261	1.601046
O	-1.1253	-2.98436	-0.99628
O	1.529804	-1.67481	-3.37783
O	3.465856	1.600618	1.471639
O	1.530822	1.675135	3.377217
O	-3.7339	3.749103	0.061328
O	-1.52989	-1.38748	3.505499
O	-1.52969	-3.37772	1.675242
O	1.530993	-3.5051	-1.38758
O	3.465612	-1.59984	-1.47306
O	2.977081	-1.08631	1.180364
O	1.125995	-0.99644	2.983806
O	1.127753	-2.89282	1.243599
O	-1.09876	0.994565	-1.08025
O	1.09859	1.080755	0.994192
O	-1.09818	-0.99471	1.080656
O	-3.73485	-0.37253	-3.73073
O	1.098345	-1.08058	-0.99466
O	3.733883	3.731654	-0.37287
O	-0.23146	3.884414	3.570948
O	-3.73335	0.371743	3.732252
O	-3.73307	-3.74997	-0.05977
O	-0.23215	-3.88443	-3.57078
O	3.732404	0.06106	-3.75056
Co	0.000008	0.000011	0.000001
W	2.530665	0.239129	2.510299
W	-0.13371	-2.41357	2.623598
W	2.530518	-2.52213	-0.02895
W	-0.13538	2.413497	-2.62355
W	-2.53068	2.510373	-0.23825
W	-2.53057	0.028149	-2.52209
W	2.529962	2.522639	0.027823
W	0.134811	2.623893	2.413245
W	-2.52944	-0.02867	2.523154
W	-2.53011	-2.51088	0.239373
W	0.13428	-2.62382	-2.41322
W	2.529641	-0.23861	-2.51142

Anion cluster 3a (doublet)

Atom	*X*	*Y*	*Z*

Si	0.024602	0.000704	-0.14757
W	0.006557	3.58749	-0.17245
O	1.241993	2.903279	-1.45315
O	0.381031	5.313252	-0.16549
O	-1.42824	3.53908	-1.46285
O	-0.88237	1.359441	-0.17409
W	-2.47424	1.964229	1.557352
O	-1.06577	1.337178	2.761639
O	-3.65404	2.639759	2.684364
O	-1.37795	3.528191	1.207308
W	-2.47544	1.928141	-1.92964
O	-3.09088	0.101364	-1.70359
O	-3.72162	2.652283	-2.96119
O	-3.32239	2.255469	-0.11042
Co	0.102572	-0.00253	-3.36901
O	-1.22094	1.349262	-3.11781
O	1.540365	1.290364	-3.6407
O	1.028703	-0.0311	-1.42378
W	2.44288	-1.77677	-2.14366
O	1.048502	-2.98232	-1.45324
O	3.633726	-2.92859	-2.76749
O	1.449663	-1.38947	-3.64157
W	2.557502	1.6121	-2.14427
O	3.034985	1.55962	-0.18427
O	3.81987	2.683485	-2.77148
O	3.456926	-0.1149	-2.2952
W	0.15679	-0.00079	3.412987
O	-1.14661	-1.26059	2.759674
O	-0.15368	0.008163	5.153031
O	1.518927	-1.38304	3.304601
O	0.952564	-0.02725	1.197088
W	2.625105	1.639989	1.654055
O	1.241548	2.890644	1.151623
O	3.888015	2.692002	2.301433
O	1.607261	1.286114	3.303598
W	2.506913	-1.80813	1.656041
O	2.912514	-1.74683	-0.18292
O	3.701522	-2.93914	2.299095
O	3.432414	-0.11223	1.945432
W	-0.22844	-3.58394	-0.17115
O	1.050254	-2.97243	1.15547

O	0.030156	-5.33102	-0.16606
O	-1.60529	-3.43528	1.210118
O	-0.95903	-1.30416	-0.17095
W	-2.5952	-1.76129	-1.92928
O	-1.30732	-1.26723	-3.11981
O	-3.88639	-2.40323	-2.95958
O	-1.657	-3.43813	-1.45998
W	-2.59191	-1.79952	1.559309
O	-2.96664	0.097677	1.518448
O	-3.8128	-2.3943	2.687914
O	-3.45856	-2.03206	-0.10748

Anion cluster 3a (quartet)

Atom	*X*	*Y*	*Z*
Si	-0.02184	0.003061	0.119102
W	0.345174	3.487851	0.813172
O	-0.97906	2.702387	1.95467
O	0.144264	5.210346	1.140512
O	1.756521	3.060616	2.065708
O	1.009022	1.241751	0.387207
W	2.686817	1.998893	-1.20705
O	1.243958	1.754087	-2.50009
O	3.939404	2.757207	-2.19294
O	1.741367	3.564879	-0.55307
W	2.647076	1.30729	2.215782
O	3.042181	-0.51652	1.661989
O	3.965364	1.697717	3.328638
O	3.535726	1.877647	0.477443
Co	-0.17424	-0.63319	3.268405
O	1.343996	0.662763	3.304972
O	-1.56081	0.795534	3.841324
O	-1.01056	-0.17638	1.407032
W	-2.70145	-1.87486	1.711991
O	-1.372	-3.03559	0.830675
O	-4.04907	-2.97831	2.005697
O	-1.76604	-1.97485	3.298912
W	-2.44065	1.468744	2.394188
O	-2.86281	1.790031	0.431788
O	-3.63723	2.542243	3.132423
O	-3.49238	-0.17471	2.198988

W	-0.09086	0.696607	-3.39549
O	1.068009	-0.78665	-2.98957
O	0.252812	1.004991	-5.09994
O	-1.57738	-0.546	-3.54996
O	-0.93847	0.308112	-1.19719
W	-2.42387	2.195828	-1.34325
O	-0.92952	3.185013	-0.60822
O	-3.56089	3.476854	-1.77191
O	-1.40611	2.066221	-3.03025
W	-2.63846	-1.17078	-2.0215
O	-3.07443	-1.40042	-0.20158
O	-3.92201	-2.03968	-2.86659
O	-3.39024	0.629846	-1.99005
W	-0.12861	-3.51244	-0.53966
O	-1.31756	-2.54799	-1.73075
O	-0.55654	-5.19062	-0.87414
O	1.274235	-3.24396	-1.87607
O	0.836427	-1.36876	-0.10065
W	2.422198	-2.33354	1.505581
O	1.193894	-2.04664	2.842008
O	3.670617	-3.27691	2.326733
O	1.298543	-3.76535	0.738563
W	2.431835	-1.68933	-1.92683
O	2.997089	0.115029	-1.52084
O	3.595726	-2.18109	-3.15911
O	3.250995	-2.3257	-0.34297
O	-0.10437	-3.28911	5.01463
H	-0.91226	-2.96437	4.532242
H	0.620805	-3.10142	4.369097

Anion cluster 4a (open-shell singlet)

Atom	*X*	*Y*	*Z*
Si	-5.8E-05	0.031217	-0.1503
W	3.594082	0.115019	-0.17149
O	2.936902	-1.17367	-1.42682
O	5.30888	-0.2224	-0.14936
O	3.497413	1.497363	-1.50897
O	1.334276	0.94473	-0.19187
W	1.877913	2.588336	1.460864
O	1.297291	1.193659	2.694215

O	2.490193	3.812743	2.548813
O	3.483295	1.541525	1.153446
W	1.842708	2.454634	-1.98513
O	-0.00348	2.993899	-1.78742
O	2.479216	3.652428	-3.09519
O	2.1496	3.398423	-0.24068
Co	0.000524	-0.26409	-3.27335
O	1.299501	1.085445	-3.09008
O	1.31849	-1.59323	-3.57981
O	0.001302	-0.94759	-1.48852
W	-1.71561	-2.5773	-2.04608
O	-2.93362	-1.18084	-1.427
O	-2.80815	-3.79938	-2.65285
O	-1.31421	-1.59644	-3.57999
W	1.722251	-2.57301	-2.04583
O	1.654319	-2.96743	-0.11379
O	2.817637	-3.79259	-2.65249
O	0.004382	-3.48444	-2.16212
W	-0.00029	-0.03092	3.397037
O	-1.30062	1.190485	2.694131
O	-0.00078	0.346935	5.103634
O	-1.32321	-1.45053	3.321669
O	0.000764	-0.93869	1.142085
W	1.721807	-2.50021	1.726012
O	2.924305	-1.09915	1.17774
O	2.810942	-3.69613	2.390156
O	1.326443	-1.44705	3.321679
W	-1.71612	-2.50437	1.725687
O	-1.64698	-2.97166	-0.11394
O	-2.8024	-3.70291	2.389749
O	0.003968	-3.36747	2.02313
W	-3.59428	0.106417	-0.17205
O	-2.92179	-1.10617	1.177524
O	-5.30822	-0.23523	-0.15023
O	-3.48721	1.53308	1.152986
O	-1.33654	0.941511	-0.1925
W	-1.84823	2.450305	-1.98542
O	-1.30181	1.082427	-3.09031
O	-2.48761	3.64665	-3.09539
O	-3.50076	1.488968	-1.5094
W	-1.88446	2.583853	1.460607

O	-0.00378	3.016306	1.391601
O	-2.49983	3.806698	2.548568
O	-2.1578	3.393321	-0.24087

Anion cluster 4a (triplet)

Atom	*X*	*Y*	*Z*
Si	-0.00036	0.007834	-0.13818
W	-3.59398	-0.13987	-0.17233
O	-2.94651	1.09816	-1.48315
O	-5.32201	0.172978	-0.17251
O	-3.47465	-1.57304	-1.46204
O	-1.32433	-0.93928	-0.16072
W	-1.86068	-2.52271	1.579923
O	-1.2918	-1.08241	2.762144
O	-2.48083	-3.71612	2.708667
O	-3.47316	-1.50562	1.207437
W	-1.83543	-2.56716	-1.8866
O	0.021148	-3.07346	-1.70793
O	-2.49462	-3.82829	-2.92221
O	-2.11921	-3.40355	-0.09513
Co	-0.00155	0.078114	-3.3365
O	-1.28304	-1.27208	-3.10018
O	-1.31674	1.386644	-3.65076
O	-0.00804	0.992513	-1.43455
W	1.6822	2.482366	-2.14536
O	2.930342	1.139993	-1.4848
O	2.771213	3.674607	-2.84285
O	1.294865	1.405323	-3.65153
W	-1.71903	2.458542	-2.1446
O	-1.67241	2.963894	-0.24297
O	-2.82529	3.63453	-2.84266
O	-0.02492	3.390898	-2.37468
W	-0.0011	0.194477	3.401633
O	1.308228	-1.06337	2.761477
O	0.001415	-0.09347	5.135017
O	1.323141	1.61683	3.272045
O	-0.00675	0.964204	1.178332
W	-1.74041	2.571719	1.626751
O	-2.93465	1.146324	1.115478
O	-2.83854	3.798131	2.237433

O	-1.34499	1.597981	3.272393
W	1.705211	2.594858	1.626146
O	1.628234	2.984852	-0.24344
O	2.785802	3.837414	2.235469
O	-0.0239	3.455609	1.877633
W	3.596278	-0.08905	-0.17497
O	2.919966	1.187824	1.114363
O	5.31972	0.248116	-0.17646
O	3.495908	-1.45585	1.205667
O	1.337974	-0.91895	-0.16173
W	1.869867	-2.54097	-1.88734
O	1.299597	-1.2535	-3.10087
O	2.546331	-3.79254	-2.9233
O	3.495944	-1.52382	-1.4636
W	1.897978	-2.49485	1.57939
O	0.021522	-2.94007	1.530573
O	2.535461	-3.67933	2.707889
O	2.167073	-3.37249	-0.09584

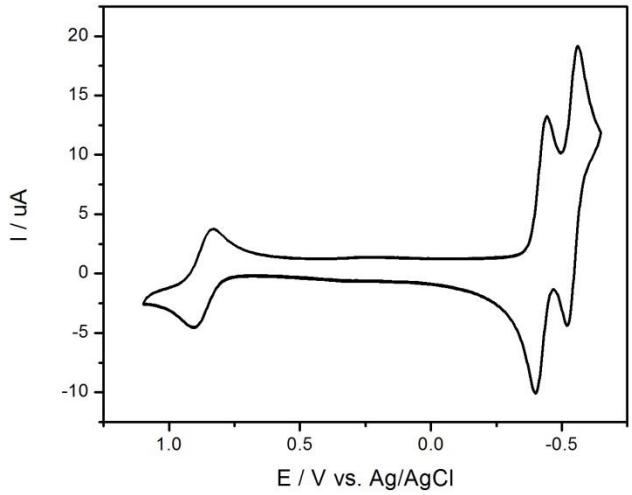

Figure S2. Cyclic voltammogram of 0.50 mM **2** recorded in 0.250 M sodium sulfate buffer, pH 2, 50 mV/s scan rate.

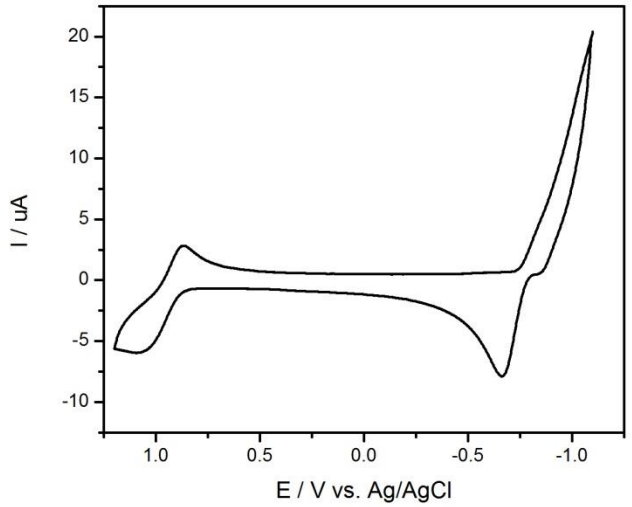

Figure S3. Cyclic voltammogram of 1.10 mM **3** recorded in 0.250 M lithium acetate buffer, pH 5, 50 mV/s scan rate.

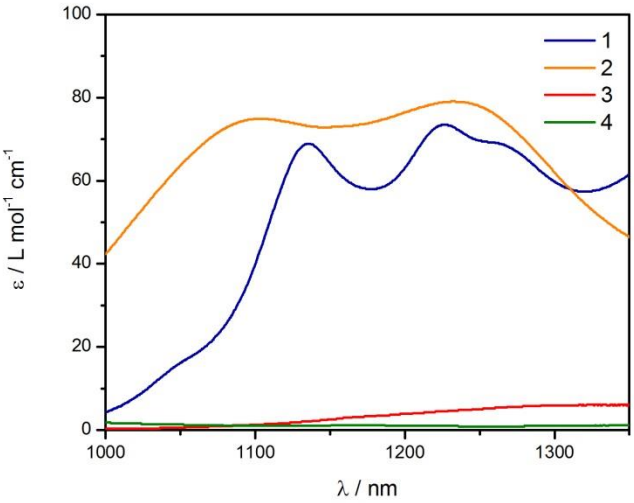

Figure S4. Near infrared electronic absorption spectra of **1**-**4** in water.

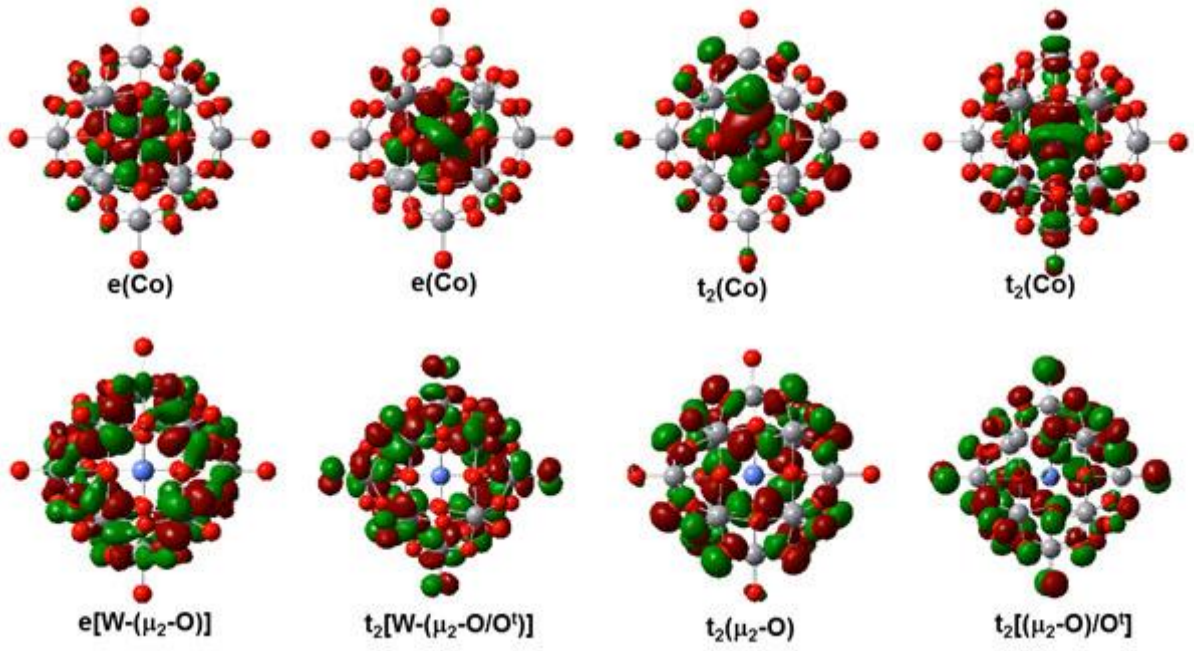

Figure S5. Important molecular orbitals for $[Co^{II}W_{12}O_{40}]^{6-}$ (**1a**) and $[Co^{III}W_{12}O_{40}]^{5-}$ (**2a**) cluster anions, discussed in this paper.

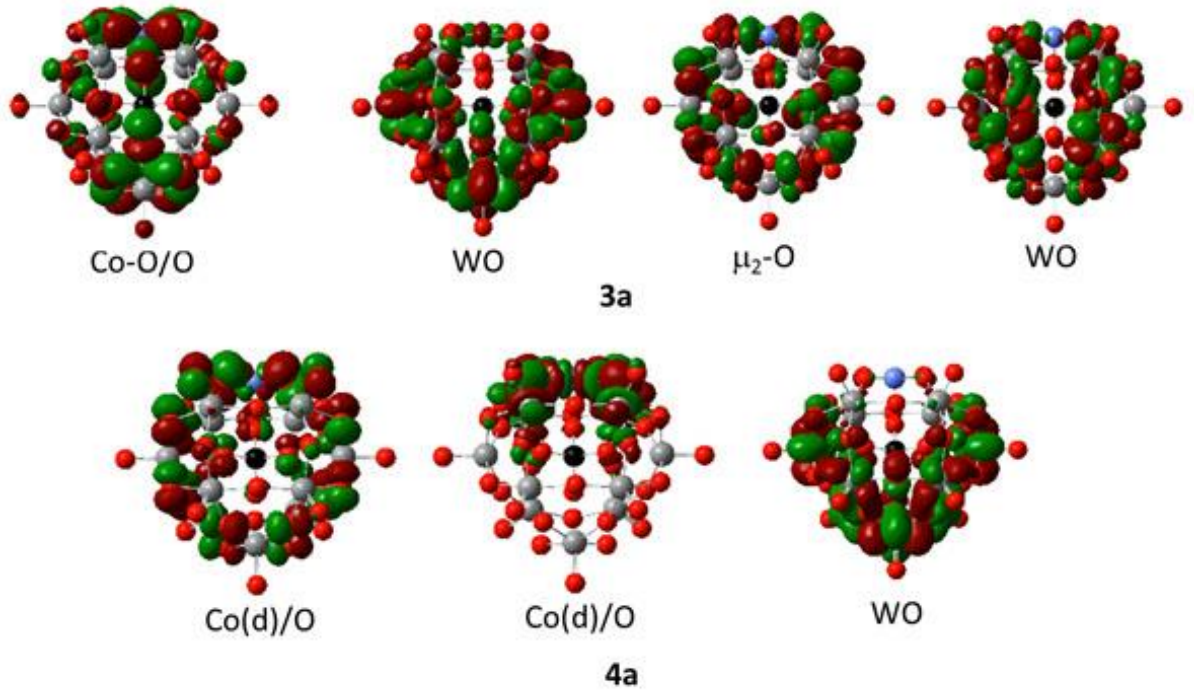

Figure S6. Important molecular orbitals for quartet anions $[SiCo^{II}(H_2O)W_{11}O_{39}]^{6-}$ (**3a**, first line) and triplet $[SiCo^{III}(H_2O)W_{11}O_{39}]^{5-}$ (**4a,** second line) cluster anions, discussed in this paper.

Table S2. Excited states of the cluster anion **1a** computed at the TD-DFT level of theory in water

state	λ / nm	osc. str. / a.u.	leading configurations
1^4T	1215	0.0000	$\{e_{CoO} \rightarrow t_{CoO}\} + \{e_{CoO} \rightarrow t_{Co\ldots W}\}$
1^4E	672	0.0000	$\{e_{CoO} \rightarrow e_{CoO}\} + \{e_{CoO} \rightarrow e_{WO}\}$
2^4E	670	0.0000	$\{e_{CoO} \rightarrow e_{CoO}\} + \{e_{CoO} \rightarrow e_{WO}\}$
2^4T	652	0.0010	$\{e_{CoO} \rightarrow t_{CoO}\}$
3^4T	565	0.0000	$\{e_{CoO} \rightarrow t_{WO}\}$
4^4T	563	0.0000	$\{e_{CoO} \rightarrow t_{WO}\}$
5^4T	513	0.0003	$\{t_{CoO} \rightarrow e_{WO}\}$
6^4T	512	0.0001	$\{t_{CoO} \rightarrow e_{WO}\}$
3^4E	454	0.0000	$\{t_{CoO} \rightarrow t_{WO}\}$
7^4T	448	0.0000	$\{t_{CoO} \rightarrow t_{WO}\}$
1^4A	443	0.0000	$\{t_{CoO} \rightarrow t_{WO}\}$
8^4T	442	0.0000	$\{t_{CoO} \rightarrow t_{WO}\}$
9^4T	431	0.0004	$\{e_{CoO} \rightarrow t_{WO}\}$
10^4T	430	0.0004	$\{e_{CoO} \rightarrow t_{WO}\}$
2^4A	429	0.0000	$\{e_{CoO} \rightarrow e_{WO}\}$
4^4E	428	0.0000	$\{e_{CoO} \rightarrow a_{WO}\}$
5^4E	425	0.0000	$\{e_{CoO} \rightarrow e_{WO}\}$

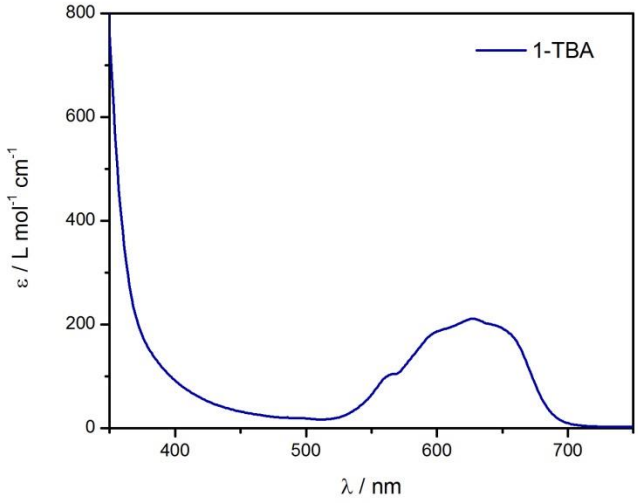

Figure S7. Visible electronic absorption spectra of **1-TBA** in MeCN.

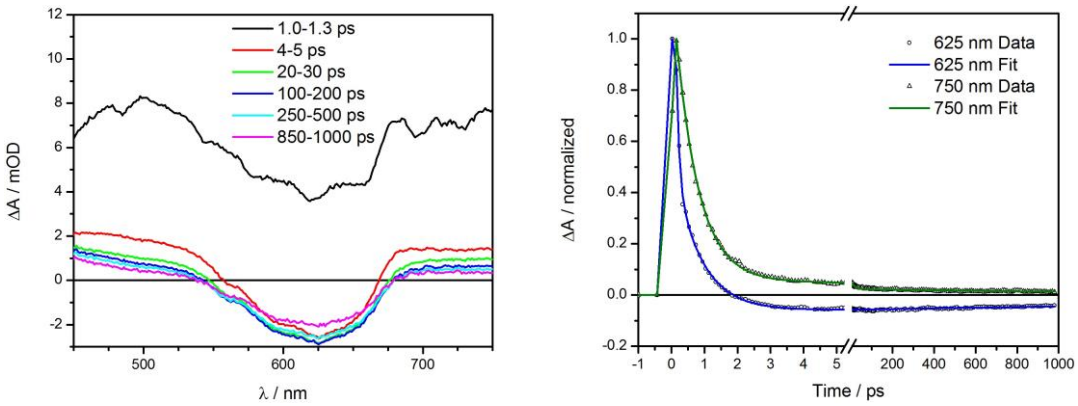

Figure S8. Transient absorption spectra (left) and kinetics (right) of **1-TBA** measured in MeCN after excitation by an ultrafast pump pulse at 400 nm. Spectral traces are the average of multiple measurements within the noted time windows. Empirical measurements and multiexponential fits to the kinetics at representative wavelengths are shown normalized to their respective peak values.

Table S3. Multi-Exponential Fit Parameters of Transient Absorption Decay Spectra at Selected Wavelengths

Compound	*Wavelength*	*Lifetimes*		*Normalized Coefficients*	
	λ (nm)	τ_1 (fs)	τ_2 (ps)	A_1	A_2
$[Co^{II}W_{12}O_{40}]^{6-}$ (**1a**)	475	710 ± 50	340 ± 50	0.89	0.11
	625	700 ± 40	430 ± 30	0.86	-0.14
	700	710 ± 40	400 ± 90	0.94	0.06
	750	790 ± 50	480 ± 100	0.94	0.06
$[Co^{III}W_{12}O_{40}]^{5-}$ (**2a**)	475	380 ± 90	5.2 ± 0.6	0.66	0.34
	600	150 ± 40	4.3 ± 0.5	0.80	0.20
	750	180 ± 60	7.1 ± 0.5	0.63	0.37
$[SiCo^{II}(H_2O)W_{11}O_{39}]^{6-}$ (**3a**)	475	580 ± 50	-	1.00	0.00
	545	260 ± 60	6.0 ± 20	0.99	-0.01
	546	570 ± 40	1.3 ± 3.8	0.99	-0.01
	600	630 ± 60	-	1.00	0.00
$[SiCo^{III}(H_2O)W_{11}O_{39}]^{5-}$ (**4a**)	470	230 ± 30	5.9 ± 0.1	0.44	0.56
	490	350 ± 130	5.8 ± 0.2	0.21	0.79
	570	980 ± 80	6.6 ± 0.2	0.44	0.56

References

[1] a) L. C. W. Baker and T. P. McCutcheon, *J. Am. Chem. Soc.* **1956**, *78*, 4503-4510; b) V. E. Simmons in *Heteropoly Tungstocobaltoates and Tungstocobaltiates based on CoO_4 Tetrahedra: Magnetic Properties, Spectra, Chemistry, and Structures*, *Vol.* Boston University, Boston, **1953**, p. 500; c) A. L. Nolan, R. C. Burns and G. A. Lawrance, *J. Chem. Soc., Dalton Trans.* **1998**, 3041-3047.

[2] J. A. Mair, *J. Chem. Soc.* **1950**, *1950*, 2364-2372.

[3] D. K. Lyon, W. K. Miller, T. Novet, P. J. Domaille, E. Evitt, D. C. Johnson and R. G. Finke, *J. Am. Chem. Soc.* **1991**, *113*, 7209-7221.