**An Infrared and Computational Investigation of Vanadium-
Substituted Keggin $[\text{PV}_n\text{W}_{12-n}\text{O}_{40}]^{(n+3)-}$ Polyoxometallic Anions**

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Supporting Information.

Table S1. Energetic characteristics, optimized coordinates, vibrational frequencies and intensities of naked anions $[\text{PW}_{12}\text{O}_{40}]^{3-}$ (reference only), $[\text{PVW}_{11}\text{O}_{40}]^{4-}$, $[\text{PV}_2\text{W}_{10}\text{O}_{40}]^{5-}$, and $[\text{PV}_3\text{W}_9\text{O}_{40}]^{6-}$ calculated at B3LYP/Lan2dz level of theory.

(35) Guo, Y.-R.; Pan, Q.-J.; Wei, Y.-D.; Li, Z.-H.; Li, X., *J. Mol. Struct.* **2004**, 676, 55-64.

Zero-point correction= 0.150670 (Hartree/Particle)
 Thermal correction to Energy= 0.208639
 Thermal correction to Enthalpy= 0.209583
 Thermal correction to Gibbs Free Energy= 0.068129
 Sum of electronic and zero-point Energies= -3835.535355
 Sum of electronic and thermal Energies= -3835.477386
 Sum of electronic and thermal Enthalpies= -3835.476441
 Sum of electronic and thermal Free Energies= -3835.617896

Center Number	Atomic Number	Coordinates (Angstroms)		
		X	Y	Z
1	74	-3.624952	0.107404	-0.133881
2	74	-1.870854	2.511147	1.658099
3	74	-1.844204	2.568416	-1.841446
4	23	-0.001074	0.018068	-3.741725
5	74	1.861343	2.556282	-1.841650
6	74	1.881891	2.503554	1.658353
7	74	-0.000735	-0.215147	3.445699
8	74	3.625169	0.087418	-0.127531
9	74	-1.724565	-2.437335	-2.136758
10	74	-1.750644	-2.613699	1.626386
11	74	1.733293	-2.625163	1.626149
12	74	1.714692	-2.444375	-2.137562
13	15	0.000037	-0.013442	-0.134244
14	8	-1.321250	0.929387	-0.110628
15	8	0.009413	3.056127	-1.679485
16	8	-3.440541	1.536468	-1.407694
17	8	0.006363	2.932831	1.603979
18	8	-1.292880	-1.334888	-3.606627
19	8	-2.947800	-1.101804	-1.457961
20	8	1.262292	1.236220	-3.014636
21	8	-1.331245	-1.607155	3.234562
22	8	1.288677	1.064532	2.814926

23	8	-2.510955	3.688731	2.765539
24	8	-2.102877	3.347599	-0.039048
25	8	-0.003027	-0.965947	1.182650
26	8	-2.800586	-3.615226	-2.831777
27	8	3.450563	1.517909	-1.402748
28	8	0.000737	0.368261	-5.295725
29	8	-1.252357	1.242888	-3.014853
30	8	-1.286378	1.070428	2.813846
31	8	-2.949791	-1.195572	1.115680
32	8	2.526409	3.677959	2.766629
33	8	-3.439009	1.454083	1.237896
34	8	-1.659554	-2.960126	-0.244304
35	8	2.943796	-1.116851	-1.453813
36	8	-0.001063	0.030135	5.167317
37	8	2.519505	3.794693	-2.871460
38	8	1.325848	0.922848	-0.109618
38	8	1.325848	0.922848	-0.109618
39	8	2.120330	3.337095	-0.037443
40	8	2.941275	-1.211414	1.119791
41	8	3.444285	1.436515	1.242643
42	8	-2.818296	-3.846812	2.227948
43	8	-0.001801	-0.954860	-1.438406
44	8	-2.494521	3.810226	-2.872071
45	8	1.289683	-1.340426	-3.605574
46	8	5.336539	-0.218891	-0.131972
47	8	-0.010699	-3.433806	1.849755
48	8	-0.006975	-3.298152	-2.368580
49	8	1.644605	-2.969460	-0.243476
50	8	1.319132	-1.614883	3.235719
51	8	2.785552	-3.627529	-2.831684
52	8	2.793493	-3.864013	2.229121
53	8	-5.337885	-0.189997	-0.140948

Frequency	IR Intensity
42.6318	0.0087
72.7599	0.0006
74.9029	0.0007
75.4620	0.0446
87.7501	0.0171
88.6140	0.0197
99.5349	0.0766
103.9569	0.0066
108.1356	0.1703
113.4057	0.2414
115.2058	0.0159
126.0547	0.0001
127.7012	0.0374
134.1015	0.2505

144.3411	0.3019
147.0013	0.0211
152.6463	0.0029
153.0508	0.0032
159.1817	0.1446
159.2719	0.1567
163.2312	0.5651
168.9710	0.1836
172.2422	0.1505
183.2673	0.0018
184.3500	0.6885
184.6311	0.2259
186.0154	0.1287
187.6962	0.0408
188.5147	0.6157
188.7548	0.8800
189.8112	0.4967
200.7158	0.6433
202.0015	0.6913
205.7192	0.0027
207.1827	0.2099
208.3760	0.5563
211.2305	0.1221
211.3183	0.2824
213.4442	0.2750
214.6176	0.1928
215.7650	0.0990
217.2310	0.1226
218.1333	0.6341
218.5865	0.3716
220.3200	0.2713
226.3060	0.1592
227.4595	0.0746
229.0684	0.0097
230.4135	1.7894
232.2075	0.2315
235.2696	1.4582
236.4254	3.0487
238.6225	3.7840
241.1362	0.7079
241.5682	0.4725
253.1657	4.0576
257.1558	0.1326
260.1476	2.8810
262.8105	22.2432
265.1306	41.7345
270.1853	34.6997
272.4496	0.1076
273.8195	15.3570
280.4366	7.3970
280.5374	14.0251

297.4461	2.5136
297.7848	1.8551
305.0443	8.9941
319.0221	0.9200
320.0884	0.3604
322.3413	0.0485
336.7025	0.6663
338.2610	0.3603
342.7372	5.1147
343.9782	1.3346
347.1682	3.6955
361.5480	0.0404
370.5085	0.0161
374.4790	4.2897
383.8487	17.7701
383.9058	18.8932
389.4364	13.4445
402.2855	26.2363
402.4599	8.0169
411.6717	24.7404
416.6672	221.2744
417.2113	269.1155
425.0585	241.7554
447.7004	3.5623
451.4878	45.3660
455.7597	14.1569
461.1789	8.9893
465.3450	8.0886
468.6833	0.1885
471.4256	6.4901
481.7416	36.3304
488.7718	0.3048
498.0757	12.1985
499.0725	15.0457
500.3968	79.4028
502.9057	45.5487
507.0820	0.3089
511.6660	10.7951
514.5316	37.0746
517.8835	16.0426
522.7791	15.4236
525.2775	26.2644
526.4414	24.4829
527.1136	20.0807
536.9311	8.7937
539.0475	3.8121
546.5888	53.2972
550.0479	35.4845
553.5344	30.0445
556.1517	1.2547
562.7867	1.6341

563.6184	1.0974
578.1761	0.8535
582.0389	6.8350
587.2232	0.0432
592.0083	11.3547
599.3554	20.1232
604.5985	5.8403
622.3594	0.0256
626.5434	1.4857
631.1952	13.8897
831.8372	2062.9282
832.4396	2043.9548
833.3516	2100.0227
877.4555	11.2904
899.6139	575.9838
903.1634	543.5102
904.4271	624.1868
907.4728	49.7116
908.8938	17.8710
913.5748	18.0340
915.3787	1.7022
917.1487	61.5848
945.9041	872.9109
946.2724	873.9568
954.2548	608.1690
963.4604	415.1415
964.0878	357.8322
965.7881	229.8385
967.7005	42.2755
968.6953	8.9455
970.0682	17.2681
970.3826	0.0900
979.0846	52.2210
1015.1300	236.4298
1016.3008	222.6669
1032.1552	389.4048
1083.1695	218.2310

Zero-point correction= 0.150116 (Hartree/Particle)
 Thermal correction to Energy= 0.208077
 Thermal correction to Enthalpy= 0.209021
 Thermal correction to Gibbs Free Energy= 0.067803
 Sum of electronic and zero-point Energies= -3838.784647
 Sum of electronic and thermal Energies= -3838.726686
 Sum of electronic and thermal Enthalpies= -3838.725742
 Sum of electronic and thermal Free Energies= -3838.866960

Center Number	Atomic Number	Coordinates (Angstroms)		
		X	Y	Z
1	74	-3.018377	1.743572	1.174036
2	74	-2.935220	0.000570	-1.852695
3	74	-3.018562	-1.743932	1.173730
4	23	-0.108784	-1.645561	3.444615
5	74	0.060263	-3.587649	0.271242
6	74	0.183189	-1.885949	-2.791487
7	74	0.183758	1.884984	-2.791621
8	74	2.943008	-1.872149	-0.678494
9	23	-0.106431	1.651751	3.440229
10	74	0.061178	3.588028	0.269408
11	74	2.943479	1.871004	-0.677869
12	74	2.692500	-0.001112	2.590244
13	15	0.008587	-0.000159	0.261888
14	8	-1.616804	0.000133	0.187166
15	8	-1.756358	-2.951546	0.358415
16	8	-3.746594	0.000420	1.615588
17	8	-1.614796	-1.284068	-2.460322
18	8	-0.404470	0.000399	4.145639
19	8	-1.821099	1.642856	2.593884
20	8	0.273724	-2.899756	1.967508
21	8	-0.120629	3.428556	-1.716133
22	8	0.526393	0.000380	-3.075895
23	8	-4.110846	0.001206	-3.146277

24	8	-3.629692	-1.323965	-0.664279
25	8	0.570072	1.324609	-0.503268
26	8	-0.349309	2.646746	4.674495
27	8	1.972221	-3.434908	-0.109437
28	8	-0.351643	-2.641375	4.678251
29	8	-1.822763	-1.644106	2.593626
30	8	-1.614499	1.286098	-2.459939
31	8	-1.754681	2.951820	0.360487
32	8	0.090185	-2.528321	-4.415018
33	8	-3.628711	1.326182	-0.663791
34	8	0.275315	2.899141	1.967776
35	8	3.012150	-1.284022	1.129321
36	8	0.091217	2.528404	-4.414750
37	8	-0.108643	-5.313364	0.506351
38	8	0.569664	-1.324968	-0.503323
39	8	-0.121591	-3.427979	-1.717226
40	8	3.148267	-0.000210	-1.102354
41	8	2.076444	-2.104370	-2.398533
42	8	-0.107463	5.313573	0.505294
43	8	0.518647	-0.000244	1.777808
44	8	-4.285196	-2.811292	1.736579
45	8	1.734550	-1.326340	3.546658
46	8	4.538623	-2.520527	-0.975923
47	8	1.972921	3.434455	-0.107950
48	8	1.734190	1.325230	3.546924
49	8	3.011803	1.282966	1.130097
50	8	2.076933	2.105182	-2.397485
51	8	4.239083	-0.001021	3.411897
52	8	4.539276	2.519232	-0.974686
53	8	-4.283993	2.811629	1.737796

Frequency	IR Intensity
40.4799	0.1017
71.0939	0.1529
77.3180	0.0746
77.8154	0.0167
89.1170	0.0105
89.4680	0.2025
96.6857	0.0835
104.1046	0.9135
107.2907	0.0437
109.3067	0.6270
116.3870	0.1401
121.1136	0.0157
129.0748	0.0815
136.2510	1.6676
145.5183	0.5124
147.9786	0.0936
149.8025	0.2191

153.9540	0.0336
160.3592	0.0672
160.5520	0.0754
165.6687	0.7217
172.9584	0.5292
173.4358	0.0428
179.9462	0.0081
182.4609	0.8541
183.1650	0.2146
185.6325	0.1682
186.9512	1.6267
188.3027	0.4352
188.8427	0.7606
190.4156	1.4098
200.0201	0.2507
200.6587	0.0070
205.6211	0.1094
206.3778	0.0429
209.4831	0.0300
210.1290	0.1995
212.4361	0.0358
214.1985	0.0961
214.6686	0.0658
217.4299	0.2421
218.4286	0.3609
221.8028	0.0715
222.3267	0.1370
223.4724	1.0738
226.1725	0.0669
229.9545	0.9535
231.7143	1.0592
232.4015	1.5532
234.8160	4.5365
237.3313	0.2305
240.2864	5.2779
243.9948	4.2411
245.6001	2.9545
248.8738	0.0221
258.6348	0.0971
262.0214	9.1464
265.0180	25.1111
266.4881	28.0627
272.3441	9.7607
272.4463	8.2762
275.5584	9.3387
279.1581	6.6787
282.0332	51.4265
289.2058	3.4520
297.9470	2.3330
302.6901	13.5909
304.4445	0.1451

315.8121	0.5328
319.2252	0.3766
325.5168	1.1278
334.6276	0.7038
336.9730	0.2816
341.2301	7.6458
342.5007	0.4936
345.8471	5.5259
351.0649	0.2152
370.4500	2.7658
374.6683	1.0687
383.6686	7.5436
385.6117	21.1356
386.5266	4.9683
400.7059	58.3024
408.1098	5.8963
411.7450	23.1436
414.4912	214.1171
416.3395	290.4352
427.0692	188.2934
433.5449	60.0583
446.7012	4.9451
453.2098	29.4890
457.3039	0.6015
463.2545	0.6618
463.5331	13.3412
468.2762	1.9133
473.4841	9.5820
474.9813	12.0519
491.0414	15.9798
493.5713	33.1978
494.5183	17.8272
500.7388	2.5657
501.8965	18.4166
506.6511	55.1641
508.6523	16.6893
510.5898	62.5461
517.6739	28.6832
522.4345	16.8055
524.8066	28.4456
530.5069	20.6750
534.1055	39.7116
543.5418	6.8078
545.4044	48.7674
549.1847	21.3819
555.3551	1.8870
558.4761	45.4060
563.9043	0.1515
566.1254	10.6613
581.6719	5.3058
586.8435	11.7963

587.6302	10.0147
596.0212	0.2586
605.1223	39.8657
606.0430	4.0472
619.8107	0.2099
644.1133	12.8605
656.7507	33.3467
820.5083	2025.5401
822.6654	2132.3163
822.9164	2018.2186
872.2942	11.3175
889.1019	558.1152
889.2623	656.4763
893.5049	104.4879
894.3242	515.0781
896.9507	237.6400
898.2454	52.4897
900.1749	32.6756
901.6737	8.6534
926.4911	857.7078
927.5129	759.3731
939.0737	514.3408
944.8019	463.3708
945.7545	176.5064
949.2705	125.2348
951.1987	10.8544
952.9646	3.9970
953.4209	5.3047
958.5341	129.9460
1001.9691	254.8552
1002.8644	271.0837
1030.8244	660.1845
1046.6996	272.4675
1072.8288	94.1480

Zero-point correction= 0.149764 (Hartree/Particle)
 Thermal correction to Energy= 0.207631
 Thermal correction to Enthalpy= 0.208575
 Thermal correction to Gibbs Free Energy= 0.068114
 Sum of electronic and zero-point Energies= -3841.926283
 Sum of electronic and thermal Energies= -3841.868416
 Sum of electronic and thermal Enthalpies= -3841.867471
 Sum of electronic and thermal Free Energies= -3842.007932

Center Number	Atomic Number	Coordinates (Angstroms)		
		X	Y	Z

1	74	2.487111	2.607648	0.381936
2	74	0.527914	2.111813	-2.469516
3	74	-0.892310	3.478355	0.428468
4	23	-1.413168	1.258557	3.420212
5	74	-3.501621	0.849815	0.385106
6	74	-2.096631	-0.601652	-2.466705
7	74	1.566255	-1.516885	-2.467195
8	74	-2.565777	-2.511634	0.434816
9	23	1.795100	0.602368	3.419891
10	74	3.459243	-0.966908	0.431870
11	74	1.014022	-3.456834	0.386212
12	23	-0.376892	-1.846470	3.422667
13	15	-0.001044	0.000109	0.410744
14	8	0.383166	1.480437	-0.166941
15	8	-2.437803	2.405174	-0.024105
16	8	1.012433	3.851752	0.602259
17	8	-1.060932	1.036134	-2.668102
18	8	0.384528	1.449735	4.026551
19	8	2.212518	1.935862	2.091995
20	8	-2.779614	0.946672	2.093503
21	8	3.213874	-1.303741	-1.538346
22	8	-0.369702	-1.440137	-2.670346

23	8	0.714506	2.838766	-4.059971
24	8	-0.480301	3.432911	-1.539812
25	8	1.086113	-1.076188	-0.166912
26	8	2.932447	0.887332	4.533505
27	8	-3.842961	-1.049862	0.605685
28	8	-2.227691	2.103098	4.532917
29	8	-0.978302	2.736744	2.099688
30	8	1.430287	0.398125	-2.670001
31	8	3.298270	0.907236	-0.024704
32	8	-2.821520	-0.803173	-4.056174
33	8	2.090223	2.761406	-1.551908
34	8	2.862192	-0.519953	2.102689
35	8	-1.879678	-2.212452	2.104353
36	8	2.102701	-2.044333	-4.056791
37	8	-5.123117	1.513067	0.548618
38	8	-1.478317	-0.407737	-0.160349
39	8	-3.437627	0.429588	-1.549602
40	8	-0.864735	-3.314850	-0.021231
41	8	-2.735794	-2.133442	-1.535763
42	8	5.197807	-1.181324	0.609262
43	8	0.003647	0.001794	2.002908
44	8	-1.574526	5.091667	0.606972
45	8	-1.441004	-0.386252	4.028630
46	8	-3.621415	-3.908988	0.616952
47	8	2.830460	-2.801692	0.605507
48	8	1.062215	-1.049778	4.029641
49	8	0.570778	-2.874909	2.092671
50	8	1.346494	-3.194041	-1.548957
51	8	-0.699782	-2.974284	4.535740
52	8	1.250301	-5.192332	0.554509
53	8	3.873923	3.678314	0.543674

Frequency	IR Intensity
53.7803	0.3723
79.6473	0.2087
79.9336	0.2315
83.0259	0.7273
86.0277	0.4130
86.5730	0.3712
102.0515	0.2491
102.6678	0.2573
108.8451	0.0186
113.8063	0.0356
114.9656	0.7172
115.3980	0.7046
135.0425	0.3202
135.4508	0.3460
148.4848	0.4911

148.8604	0.2073
149.0074	0.3281
154.1770	0.5548
162.6898	0.1763
162.7568	0.2012
165.3973	0.0080
176.5002	0.6276
177.0708	0.2684
178.2550	0.3931
179.9369	0.6748
180.3875	1.2487
184.8042	0.5102
185.5743	3.6408
186.1416	0.7262
191.4371	0.8353
193.0039	0.7540
196.0821	0.0911
202.3273	2.8929
204.7822	0.1455
204.8475	0.1312
209.6871	0.0645
210.5245	0.0794
212.1668	0.2081
212.4741	0.1442
213.5307	0.0304
216.7647	0.5400
222.1530	1.2624
222.5237	1.3801
223.8957	0.5820
228.4011	0.1812
228.5670	0.3193
230.0263	0.0927
233.2158	0.2636
233.6207	0.2434
238.5822	0.5737
241.3755	14.5742
245.3570	1.1685
245.4142	1.0825
249.7057	5.1505
250.2025	4.9990
257.6047	1.3916
266.8805	34.0262
267.7022	33.3242
272.0202	0.6827
273.5514	5.7952
277.5121	16.7111
277.7551	17.2168
283.5397	49.9556
286.9748	3.1598
287.5627	1.5131
298.8676	6.0231

299.7138	5.6557
303.2500	1.8547
319.5772	0.2214
321.6371	1.1851
321.9330	1.1522
335.4423	0.5855
337.3095	0.9351
338.5989	12.6692
345.1555	0.1175
346.7207	0.3484
350.4541	6.7566
368.5141	2.6436
370.0040	3.4672
383.4557	1.1919
383.8640	0.9632
384.8745	17.6944
402.4464	0.1144
407.1509	0.7363
407.2353	1.9009
415.1450	344.7965
416.3567	346.1243
420.0227	124.0753
432.9300	38.7315
445.9108	12.9473
453.7351	10.4683
454.0312	10.1103
460.0275	14.1252
461.0987	0.6860
461.2213	0.8298
467.3038	1.9581
471.5571	23.9598
471.9804	22.2996
490.9828	37.6119
491.1530	34.4969
491.3860	12.8085
499.9440	6.4223
500.4035	6.5050
506.1597	25.4954
507.1190	26.2597
509.0214	15.2859
513.7013	30.3338
522.2401	47.1360
522.6379	48.8009
532.7971	21.8757
541.4347	29.2838
544.5438	31.3368
551.5213	0.2075
553.7219	33.1175
561.9885	4.4111
562.9512	4.7309
578.6038	1.6492

583.2132	12.7858
584.6283	12.7043
602.0641	0.3915
625.0844	37.1597
625.8229	38.8497
631.6442	88.3991
659.2255	42.6515
672.5269	36.1935
672.9603	40.7225
810.0261	1894.7429
820.8852	2172.0931
821.1741	2159.2154
860.2400	27.6098
875.8376	469.3707
876.6393	493.8086
879.9449	8.5514
881.3586	80.7468
881.6784	69.6558
885.7251	596.4342
890.7852	325.1684
891.1196	331.8171
905.6181	644.8654
906.0694	625.6100
924.3407	618.5310
927.3330	164.5645
927.6085	168.8792
934.3506	101.2242
936.0254	16.2289
936.4355	69.8334
936.5924	13.4439
986.2356	298.5753
986.9458	303.5158
1013.4193	845.1498
1013.9323	316.0354
1014.1838	342.5105
1068.0295	0.0121