Electronic Supplementary Information for Dalton Transactions

Supplementary Information

$\{[V^{IV}_{14}V^{V}_{4}O_{42}(H_2O)][Ni(C_4N_3H_{13})(C_4N_3H_{14})]_4(H_2O)_6\}^{4+}$: A novel nanosized calix-type polyoxovanadate cation

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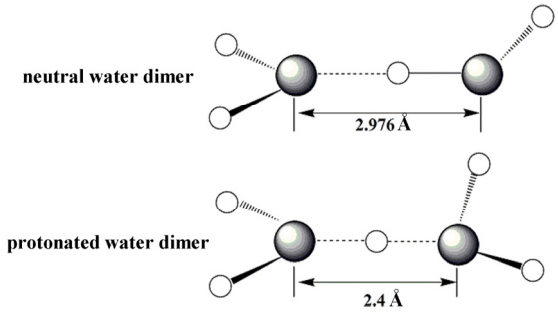


Fig. S1 Depiction of a theoretically predicted neutral and protonated water dimer.

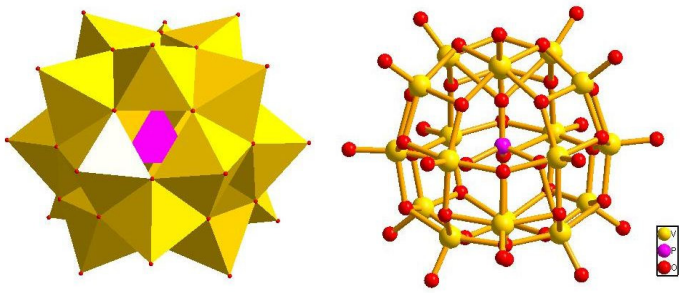
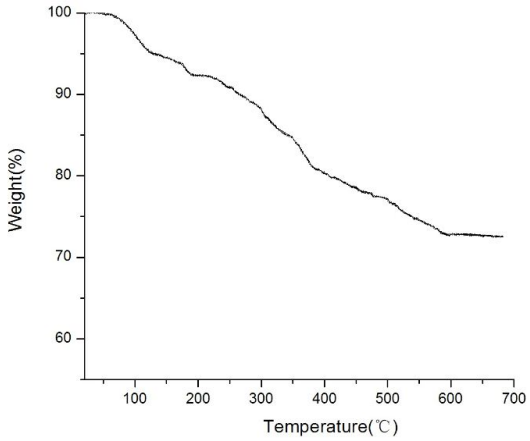
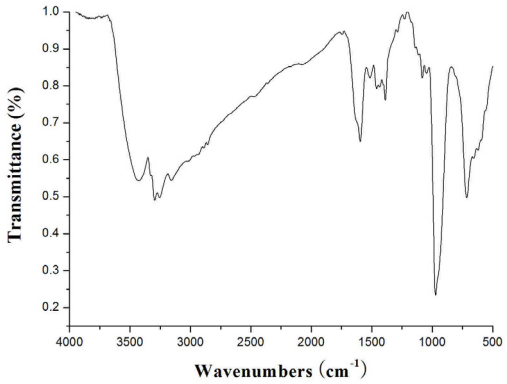


Fig. S2 Representative view of hexa-capped Keggin structural anion (Section B of **1**). (Colour code: V, gold; O, red; P, pink).



TG analysis: The weight loss of 2.55 % from 40 to 100°C are assigned to the removal of the six crystal water molecules (calculation value: 2.50 %). The weight loss of 25.09% from 100 to 610°C are attributable to the decomposition of the DETA molecule and one water molecule in the cluster (calculation value: 25.89 %) The total weight loss (27.64%) is in good agreement with the calculated value (28.39%).

Fig. S3 The TG curve of compound **1**.



IR spectrum: 3425cm^{-1}, *v*(O-H); 3296cm^{-1}, 3254 cm^{-1}, 3158 cm^{-1}, *v*(N-H); 1595 cm^{-1},1388 cm^{-1}, *v*(C-C), *v*(C-N); 1082 cm^{-1}, *v*(P-O); 972 cm^{-1}, *v*(V=O); 714 cm^{-1}, *v*(V-O-V).
Fig. S4 IR spectra of compound **1**.

Table S1 Bond valence sum for compound **1**.

V1 (×4)	3.83	V7 (×4)	4.38
V2 (×1)	4.42	V8 (×2)	4.46
V3 (×1)	4.73	V9 (×4)	4.30
V4 (×4)	4.17	V10 (×4)	4.31
V5 (×4)	4.76	V11 (×4)	4.25
V6 (×4)	4.17		

Table S2 Selected hydrogen bond lengths (Å) and angles (°).

N1—H1C···O9	0.91	2.52	3.263(5)	140
N1—H1C···O1[a]	0.91	2.32	3.095(5)	142
N2—H2C···O3[b]	0.90	2.08	2.978(5)	173
N2—H2D···O7	0.90	2.11	2.991(5)	166
N6A—H6AA···O24[c]	0.89	2.03	2.884(11)	161
N3—H3C···O14[d]	0.91	2.53	3.259(6)	137
N4—H4C···O23[d]	0.90	2.15	2.976(5)	151
N4—H4D···O4W [a]	0.90	2.43	3.224(7)	147
N6A—H6AC···O19 [d]	0.89	1.91	2.794(11)	174
N5—H5D···O14 [d]	0.90	2.48	3.265(5)	146
N6—H6C···24 [c]	0.89	1.97	2.832(13)	163
N6—H6D···O13 [d]	0.89	2.22	2.789(12)	122
N6—H6D···O19 [d]	0.89	2.19	2.924(14)	140
N8—H8C···O17[e]	0.90	2.12	3.009(8)	167
N8—H8D···O18 [e]	0.90	2.34	2.742(7)	107
O2W—H2WB···O12	0.81	2.55(1)	3.092(9)	126
N9—H9D···O11	0.89	2.41	2.799(11)	107
N9—H9E···O13[f]	0.89	2.57	3.259(12)	135
O3W—H3WB···O13[g]	0.80	2.57(1)	2.940(6)	111
O3W—H3WB···O21 [g]	0.80	2.10(1)	2.621(5)	123

Symmetry transformations used to generate equivalent atoms for **1:** [a] y, 1/2-x, z; [b] 1-y, -1/2+x, 1-z; [c] x, -1+y, z; [d] 1-x, 1-y, -z; [e] x, y, 1+z; [f] -1/2+y, 1-x, 1-z; [g] -1/2+y, 1-x, -z.