Electronic Supplementary Material (ESI) for Dalton Transactions.
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Figure S1. Thermograms for **1**, **2**, **3** and **4**.

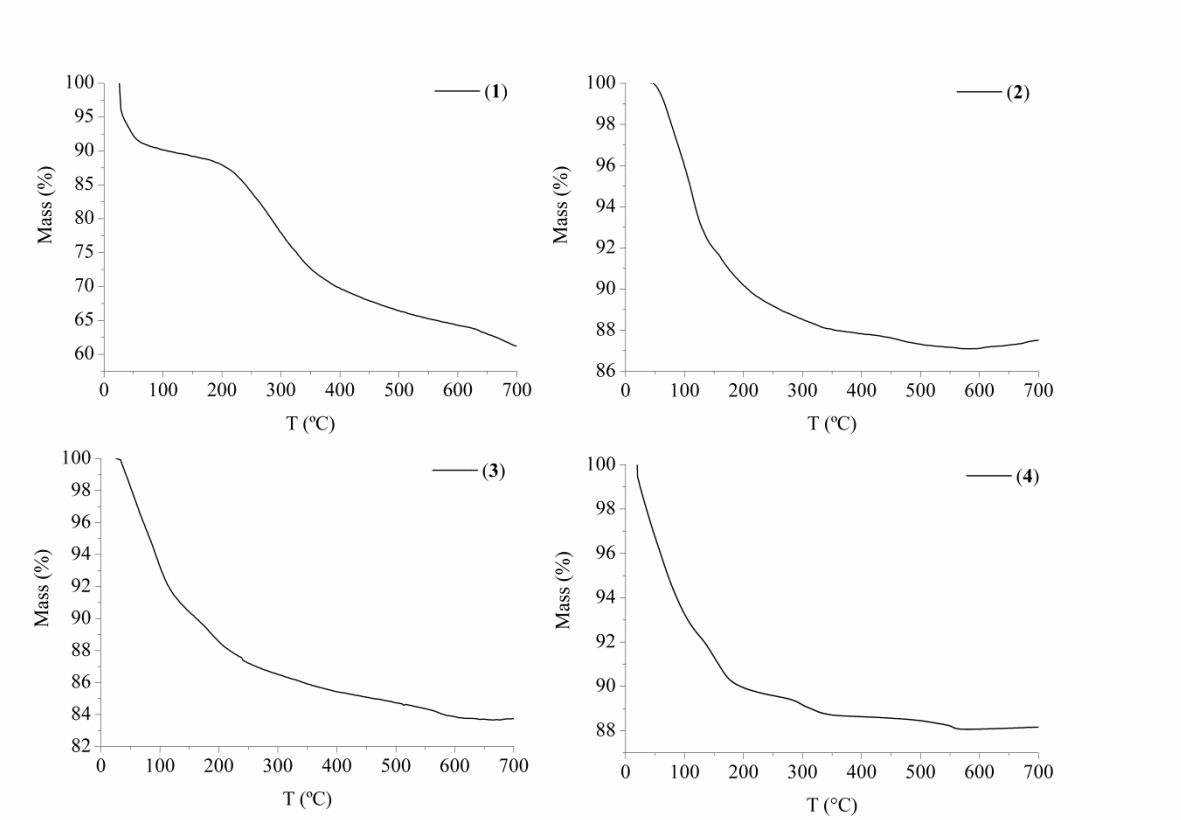

Figure S2. FTIR Spectra for **1**, **2**, **3** and **4**.

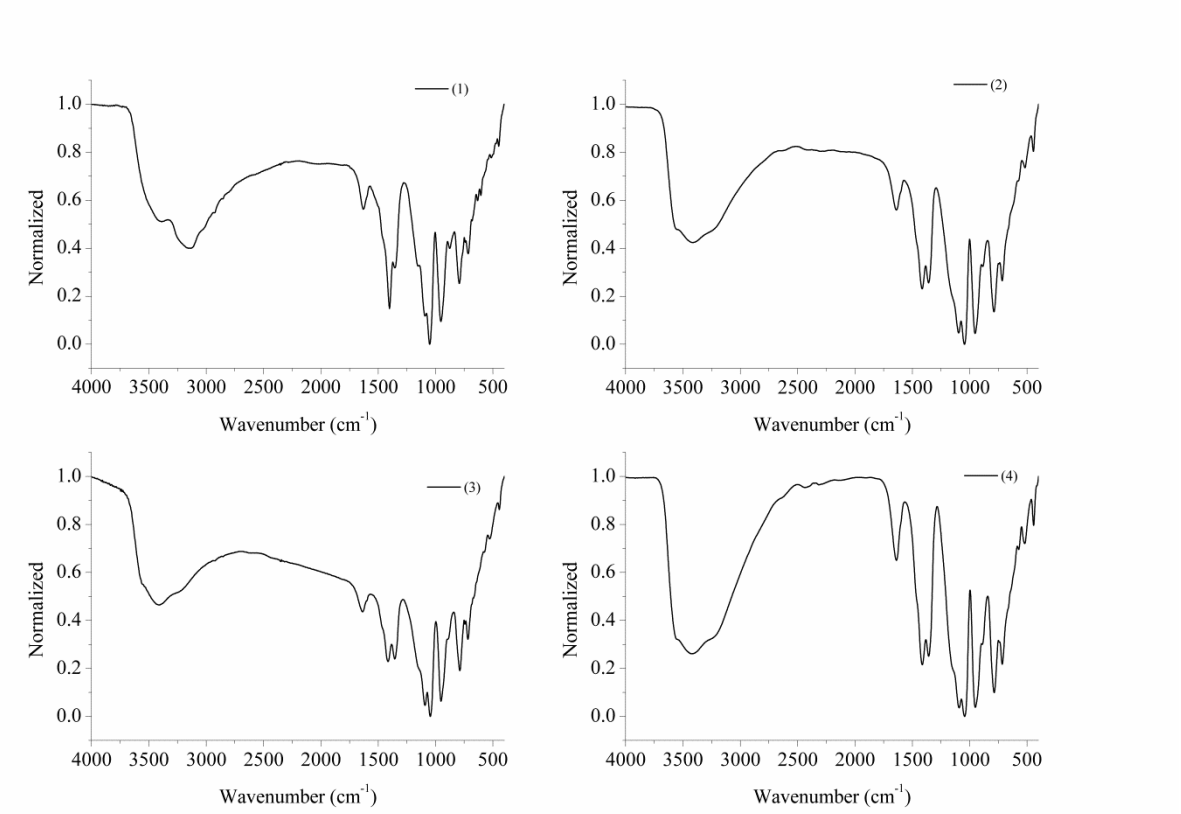

Figure S3. FTIR Spectra for **1**, **2**, **3** and **4**.

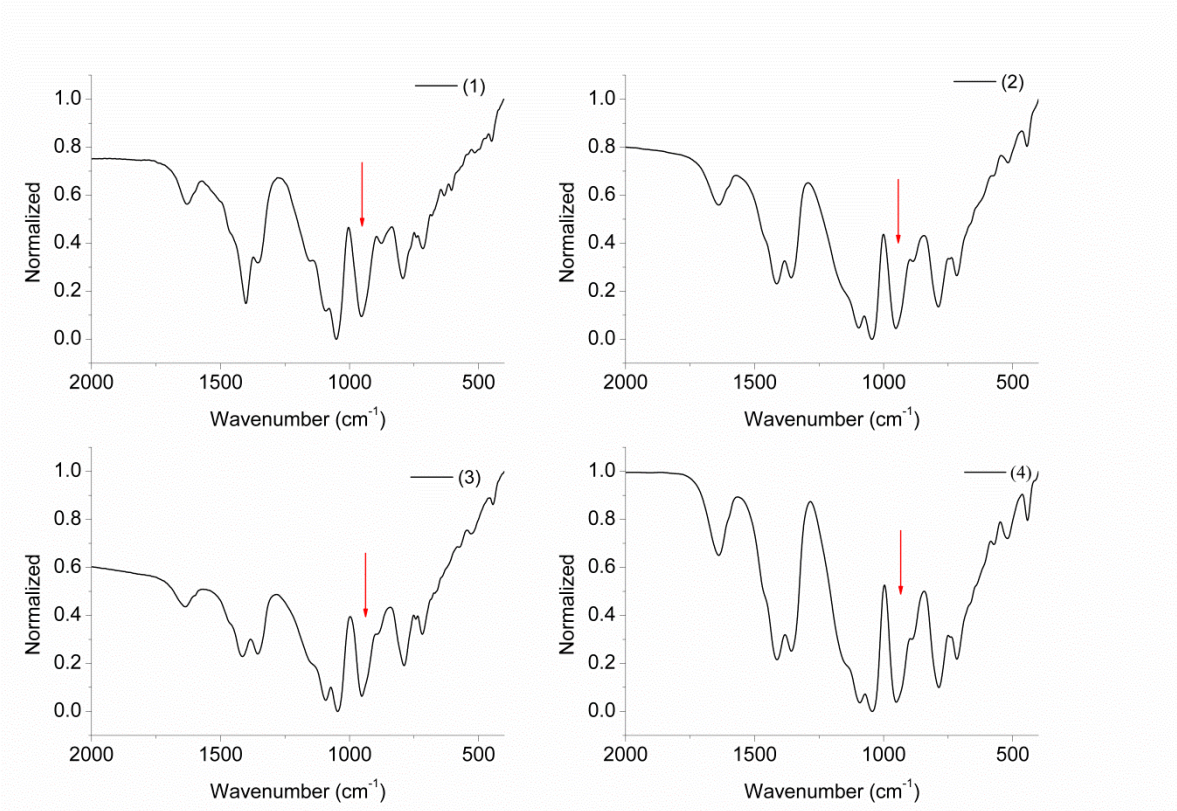

Figure S4. Scheme showing the $[V_{12}B_{18}O_{60}H_6]^{n-}$ anionic cluster.

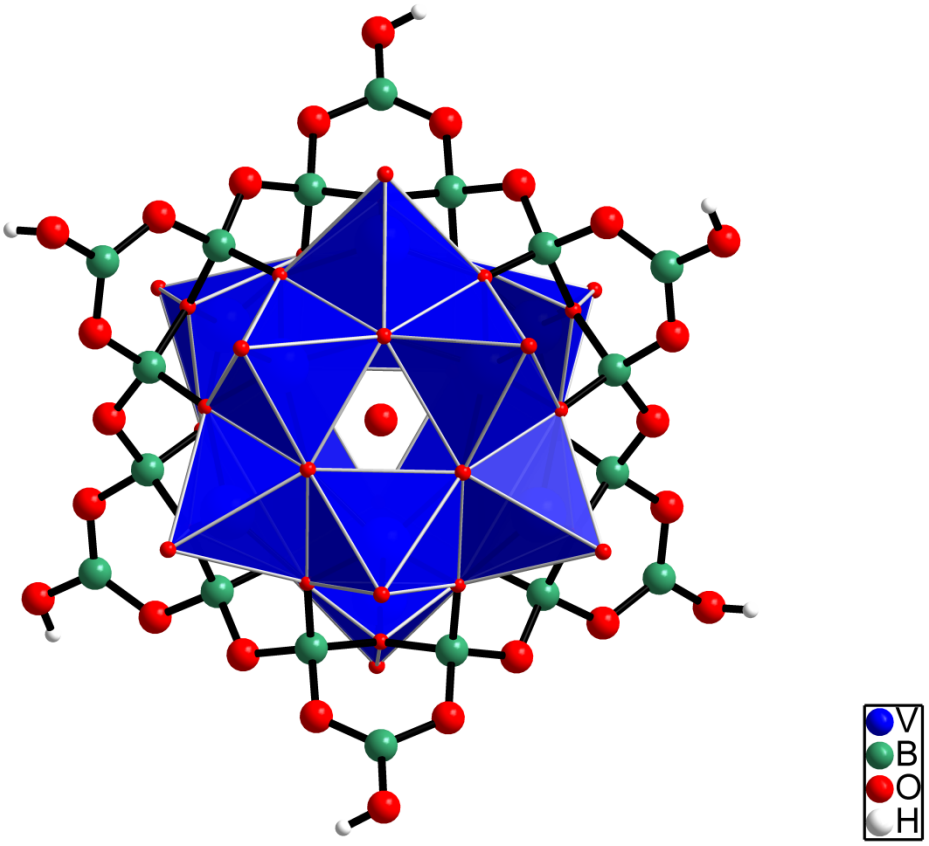

Figure S5. Detail of the different modes of hydrogen bonding in **1**.

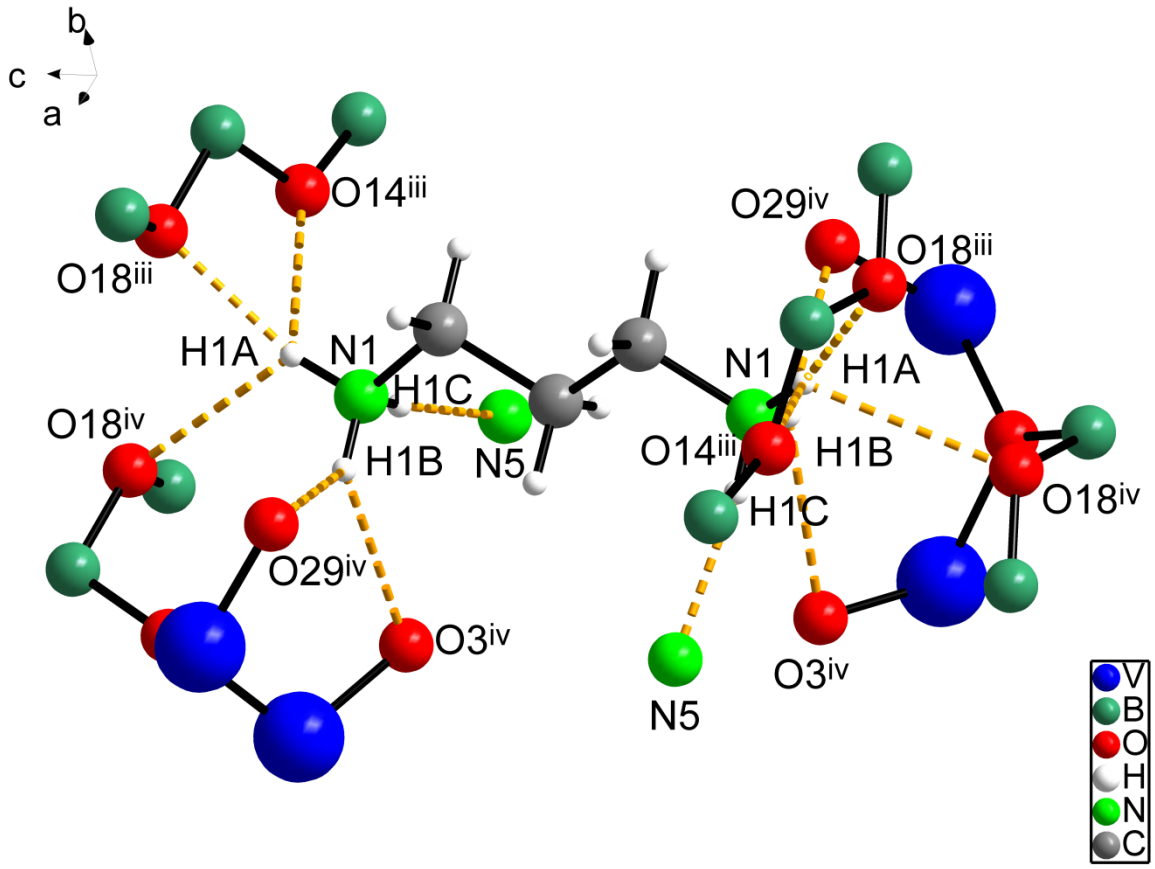

Figure S6. Scheme showing the connectivity of the 1,3-diapH_2 cation with four BVO clusters for **1**.

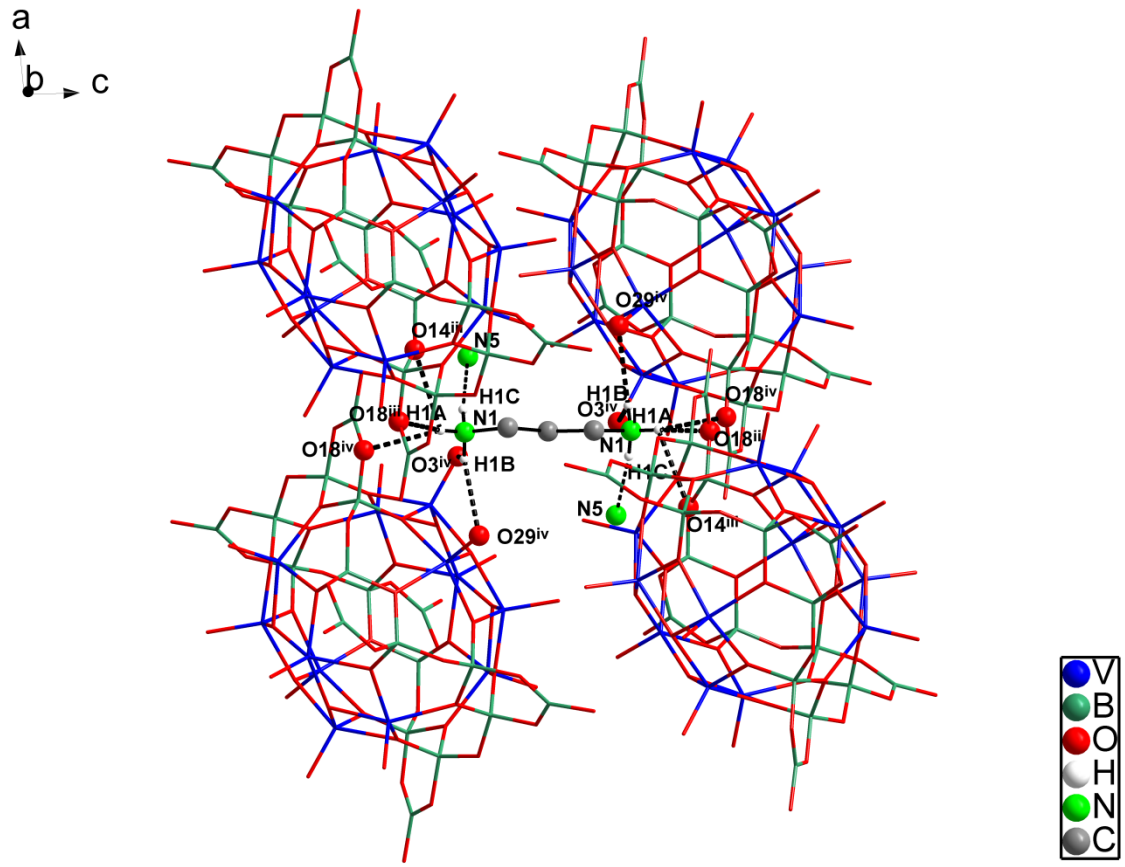

Figure S7. Donor-acceptor interactions for the ammonium ions for **1**.

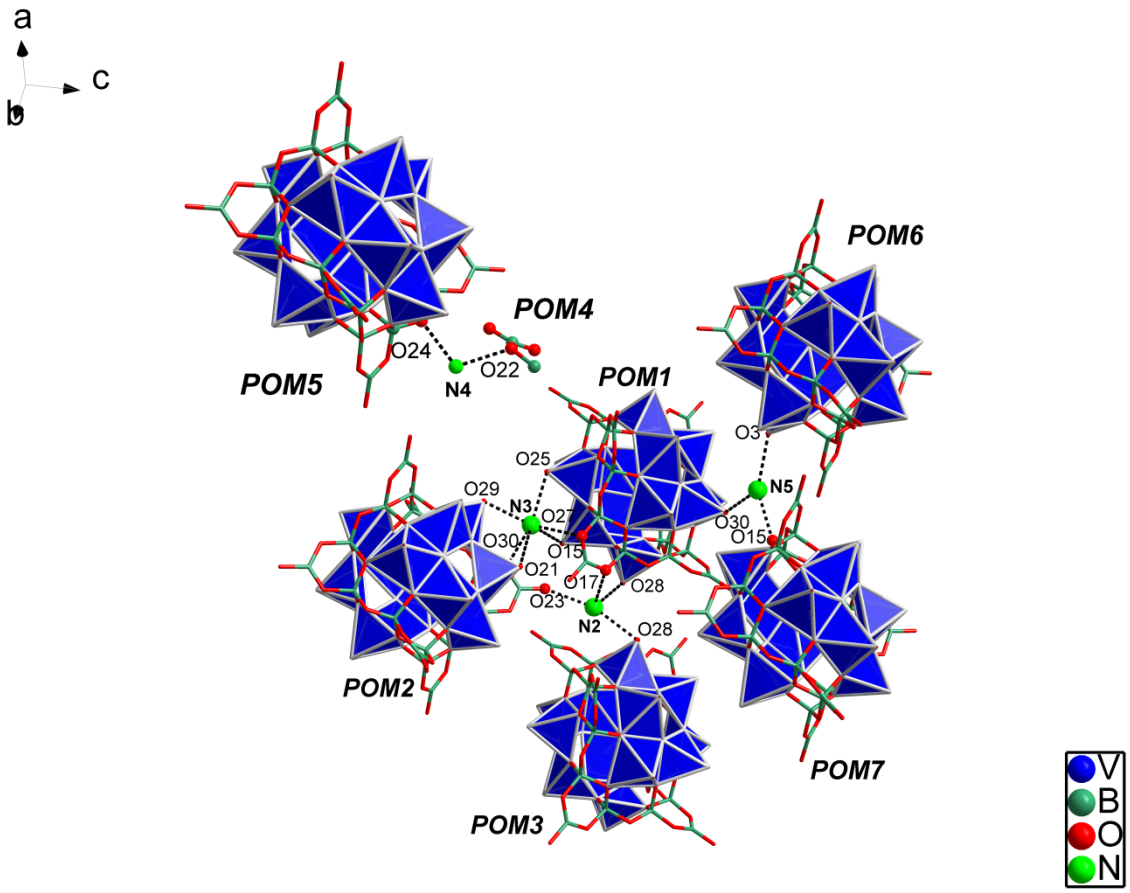

Figure S8. (a) shows the location of the alkaline ions along the *b* axis, (b) shows the alternating ABABA position of the polyanionic ligands along this same axis.

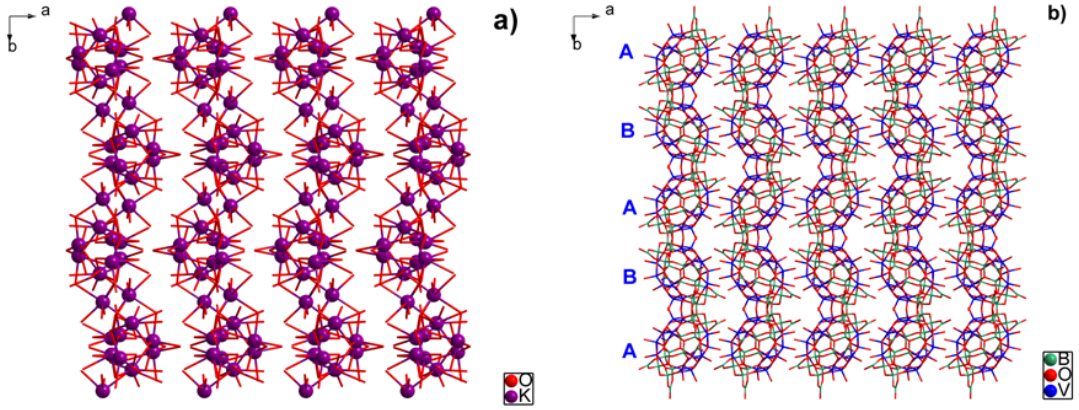

Figure S9. Shows the *ac* plane and the coordination of K1 and K4 (some of the BVO species are omitted for clarity).

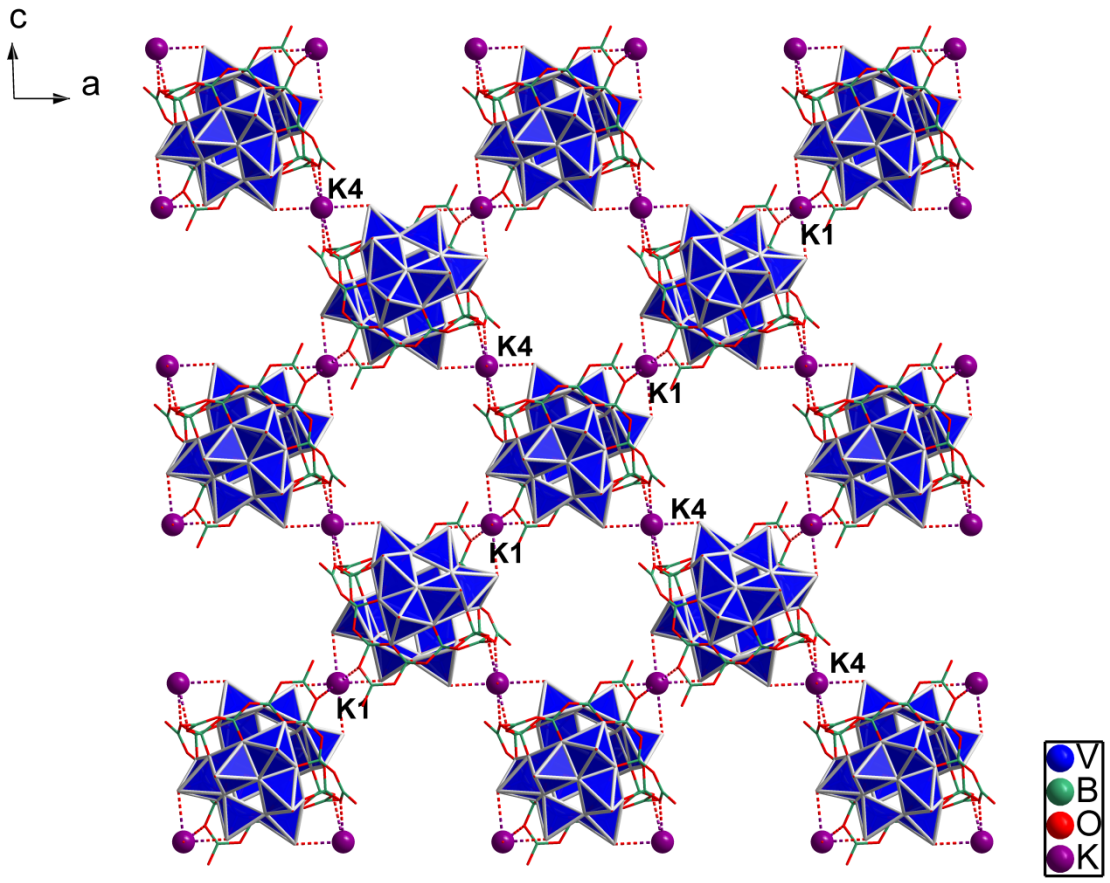

Table S1. Most relevant absorption bands in the FTIR spectra and the corresponding assignments for 1-4.

Compound	ν_{O-H}, ν_{N-H} (cm^{-1})	$\nu_{C-H\ (CH2)}$ (cm^{-1})	δ_{O-H}, δ_{N-H} (cm^{-1})	$\nu_{B-O\ (BO3)}$ (cm^{-1})	$\nu_{B-O\ (BO4)}$ (cm^{-1})	$\nu_{V=O}$ (cm^{-1})	ν_{V-O-V} (cm^{-1})
1	3388-3153	2855 (sh)	1630	1402-1355	1092-1051	954-877	793-634
2	3416	-	1639	1414-1358	1096-1045	953-886	788-640
3	3411	-	1635	1415-1356	1093-1046	952-895	779-635
4	3420	-	1639	1413-1358	1092-1044	951-890	793-638

Table S2. Hydrogen-bond geometry for 1.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*A*···O14^{iii}	0.89	2.50	2.984 (8)	115
N1—H1*A*···O18^{iii}	0.89	1.97	2.846 (8)	167
N1—H1*A*···O18^{iv}	0.89	2.53	2.995 (7)	113
N1—H1*B*···O3^{iv}	0.89	2.48	2.964 (8)	115
N1—H1*B*···O29^{iv}	0.89	2.40	3.049 (9)	130
N1—H1*C*···N5	0.89	2.03	2.910 (15)	172

Symmetry codes: (iii) x, y, 1+z; (iv) 1-x, 1-y, 1-z.

Table S3. Bond lengths [Å] for 2

K1-O11 (O11-V4)	2.688	K4-O16 (O16-V5)	2.778
K1-O16 (O16-V5)	2.756	K4-O29 (B_{tet}-O29-B_{tet})	3.003
K1-O20 (B_{trig}-O20-B_{tet})	2.860	K4-O28 (O28-B_{trig})	3.060
K1-O19 (O19-B_{trig})	2.790	K4-O3W	2.715
K1-O4W	2.916	K4-O5W	2.699
K1-O5W	2.918	K4-O6WB	2.909
K2-O17 (O17-V1)	2.923	K5-O11 (O11-V4)	3.018
K2-O18 (μ_3-O18)	2.794	K5-O15 (O15-V3)	2.874
K2-O20 (B_{trig}-O20-B_{tet})	2.752	K5-O27 (B_{trig}-O27-B_{tet})	2.788
K2-O3W	2.946	K5-O9 (O9-V6)	2.871
K2-O7W	2.795	K5-O25 (B_{trig}-O25-B_{tet})	2.725
K2-O6WA	2.789	K5-O28 (O28-B_{trig})	2.982
K3-O5 (O5-V2)	2.955		
K3-O16 (O16-V5)	2.716		
K3-O21 (B_{trig}-O21-B_{tet})	2.789		
K3-O22 (O22-B_{trig})	2.791		
K3-O3W	2.871		
K3-O12W	2.994		
K3-O9WB	2.468		

Table S4. Bond lengths [Å] for 3

K1-O3 (O3-V1)	2.936	K4-O2 (μ_3-O2)	2.829
K1-O15 (O15-V3)	3.002	K4-O7 (O7-V5)	2.871
K1-O17 (μ_3-O17)	2.782	K4-O14 (μ_3-O14)	3.047
K1-O21 (B_{trig}-O21-B_{tet})	2.983	K4-O15 (O15-V3)	2.799
K1-O22 (B_{tet}-O22-B_{tet})	2.658	K4-O24 (B_{trig}-O24-B_{tet})	2.745
K1-O1W	2.743	K4-O4W	2.940
K1-O4W	2.868	K5-O7 (O7-V5)	3.018
K2A-O4 (O4-V2)	2.777	K5-O10 (O10-V6)	2.715
K2A-O22 (B_{tet}-O22-B_{tet})	3.018	K5-O28 (B_{trig}-O28-B_{tet})	2.928
K2A-O13 (O13-V4)	2.772	K5-O27 (B_{tet}-O27-B_{tet})	2.625
K2A-O19 (O19-B_{trig})	2.854	K5-O28 (B_{trig}-O28-B_{tet})	2.846
K2A-O2W	2.900	K5-O30 (O30-B_{trig})	2.973
K2A-O4W	2.779	K5-O2W	2.859
K3-O4 (O4-V2)	2.866	K6B-O10 (O10-V6)	2.824
K3-O20 (B_{trig}-O20-B_{tet})	2.782	K6B-O18 (B_{trig}-O18-B_{tet})	3.064
K3-O20^{i} (B_{trig}-O20-B_{tet})	2.781	K6B-O19 (O19-B_{trig})	2.796
K3-O26 (B_{tet}-O26-B_{tet})	2.923	K6B-O30 (O30-B_{trig})	2.837
K3-O1W	2.993	K6B-O1W	2.914
K3-O3W	2.927	K6B-O5W	2.784

Symmetry codes: (i) 1-x, -y, 2-z

Table S5. Bond lengths [Å] for 4

K1-O15 (O15-V4)	2.708	K4-O14 (O14-V3)	3.008
K1-O28 (O28-V5)	3.171	K4-O19 (B_{trig}-O19-B_{tet})	2.744
K1-O25 (B_{trig}-O25-B_{tet})	3.009	K4-O20 (B_{tet}-O20-B_{tet})	3.093
K1-O4W	2.675	K4-O8W	2.870
K2-O16 (O16-V6)	2.749	K5-O17 (B_{trig}-O17-B_{tet})	2.772
K2-O29 (O29-B_{trig})	2.944	K5-O26 (B_{tet}-O26-B_{tet})	3.078
K2-O21 (B_{trig}-O21-B_{tet})	2.856	K5-O17^{i} (B_{trig}-O17-B_{tet})	2.752
K2-O28 (O28-V5)	2.750	K5-O11 (O11-V1)	2.871
K2-O2W	2.889	K5-O12 (O12-V2)	2.893
K2-O5W	2.843	K5-O24 (O24-B_{trig})	2.662
K2-O7W	3.064	K5-O3W	2.791
K3-O1 (μ_3-O1)	3.408	K6-O14 (O14-V3)	3.194
K3-O6 (μ_3-O6)	3.339	K6-O22 (B_{tet}-O22-B_{tet})	3.041
K3-O16 (O16-V6)	3.179	K6-O30 (B_{trig}-O30-B_{tet})	3.178
K3-O22 (B_{tet}-O22-B_{tet})	3.114	K5-O2W	2.976
K3-O30 (B_{tet}-O30-B_{trig})	3.249	K5-O6W	3.002
K3-O6W	2.766	K5-O8W	2.441

Symmetry codes: (i) 0.5-x, -0.5+y, 0.5-z

Table S6. Bond lengths [Å] for 4

Cs1A-O18 (O18-B_{trig})	3.043	Cs2-O14 (O14-V)	3.319
Cs1A-O12 (O12-V2)	2.970	Cs2-O15 (O15-V)	3.028
Cs1A-O14 (O14-V3)	3.481	Cs2-O23 (B_{trig}-O23-B_{tet})	3.264
Cs1A-O10 (μ_3-O10)	3.446	Cs2-O3W	3.031
Cs1A-O11 (O11-V1)	3.118	Cs2-O5W^{i}	3.461
Cs1A-O22 (B_{tet}-O22-B_{tet})	3.390	Cs2-O5W^{ii}	3.396
Cs1A-O23 (B_{trig}-O23-B_{tet})	3.516	Cs2-O6W	3.068
Cs1A-O7W	3.288	Cs2-O7W	3.065

Symmetry codes: (i) x, 1-y, 0.5+z, (ii) 0.5-x, -0.5+y, 0.5-z

S H A P E v2.1 Continuous Shape Measures calculation

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PP-5 1 D5h Pentagon

vOC-5 2 C4v Vacant octahedron

TBPY-5 3 D3h Trigonal bipyramid

SPY-5 4 C4v Spherical square pyramid

JTBPY-5 5 D3h Johnson trigonal bipyramid J12

Structure [ML5]	PP-5	vOC-5	TBPY-5	SPY-5	JTBPY-5
compound1-V2 ,	30.394,	2.169,	5.713,	0.457,	8.152
compound1-V1 ,	30.887,	2.316,	5.580,	0.603,	7.688
compound2-V4 ,	30.108,	2.312,	5.990,	0.600,	8.362
compound2-V1 ,	30.438,	2.117,	5.769,	0.423,	8.179
compound3-V2 ,	30.077,	2.400,	4.832,	0.670,	6.799
compound3-V3 ,	30.305,	2.190,	5.632,	0.705,	7.575
compound4-V4 ,	30.745,	2.064,	5.847,	0.467,	8.106
compound4-V3 ,	30.872,	2.375,	4.915,	0.666,	6.887