Electronic Supplementary Material (ESI) for Dalton Transactions.

Electronic Supplementary Information

Proton conduction in a new 3-D open-framework vanadoborate with an abundant hydrogen bond system

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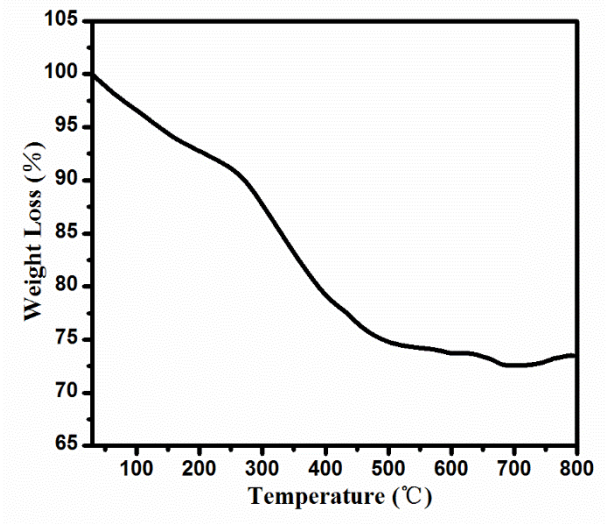

Fig. S1. TG curve of **1** in air.

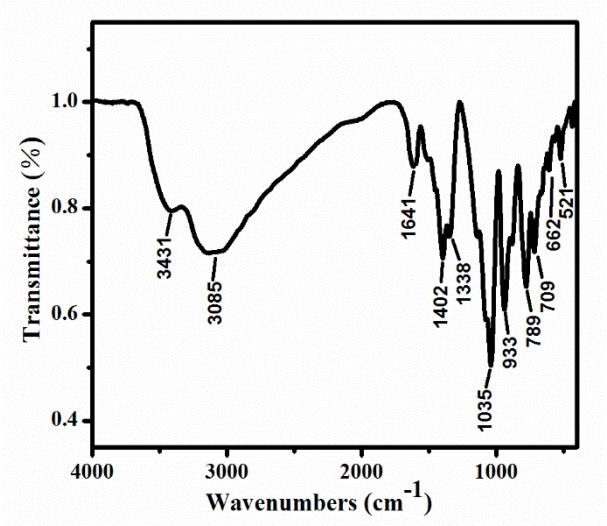

Fig. S2. The FT-IR spectrum of **1**.

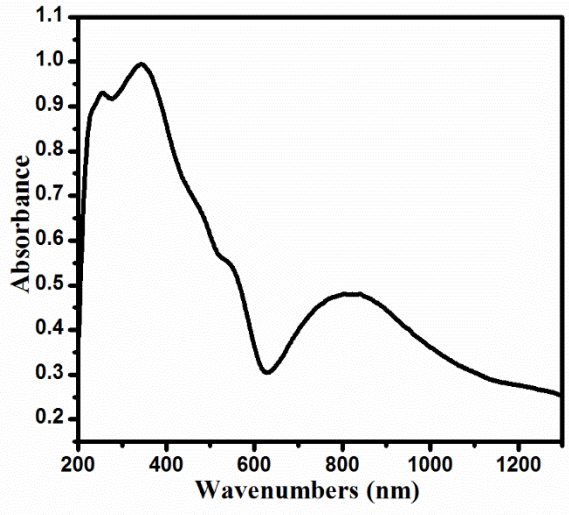

Fig. S3. UV-Vis-NIR diffuse reflectance spectrum of **1**.

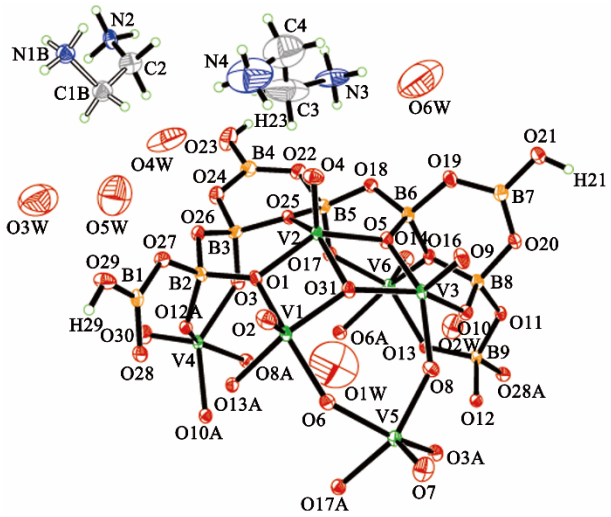

Fig. S4. The thermal ellipsoid plots (50% probability) and atomic labeling schemes of **1**.

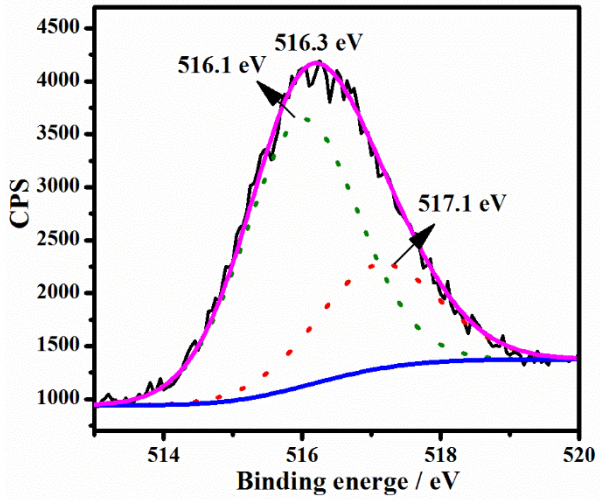

Fig. S5. XPS spectrum of vanadium in $(H_2en)_4H_2[V_{12}B_{18}O_{54}(OH)_6(H_2O)]\cdot 11H_2O$. The peak at 516.1 eV is attributed to V^{4+} and a shoulder at about 517.1 eV is assigned to for V^{5+}

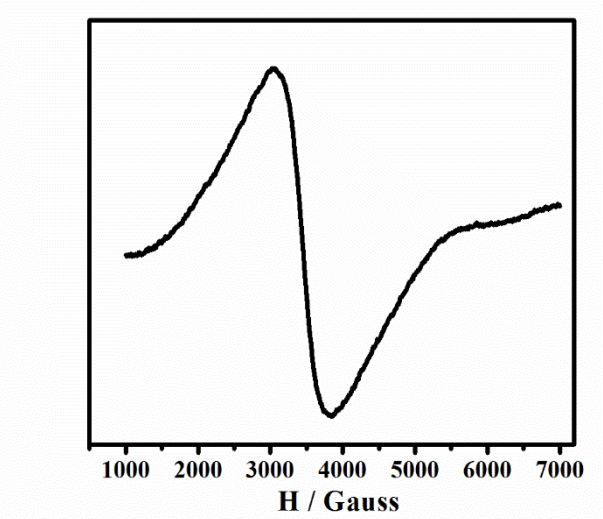

Fig. S6. EPR spectrum of **1**.

Table S1. Bond lengths [Å] for **1**.

V(1)-O(2)	1.628(3)
V(1)-O(31)	1.919(3)
V(1)-O(6)	1.920(3)
V(1)-O(1)	1.952(3)
V(1)-O(13)#1	1.950(3)
V(2)-O(4)	1.641(3)
V(2)-O(5)	1.924(3)
V(2)-O(1)	1.929(3)
V(2)-O(31)	1.940(3)
V(2)-O(25)	2.002(3)
V(3)-O(9)	1.627(3)
V(3)-O(8)	1.923(3)
V(3)-O(31)	1.922(3)
V(3)-O(5)	1.949(3)
V(3)-O(10)	1.964(3)
V(4)-O(30)	1.618(3)
V(4)-O(3)	1.933(3)
V(4)-O(8)#1	1.950(3)
V(4)-O(10)#1	1.957(3)
V(4)-O(12)#1	2.013(3)
V(5)-O(7)	1.626(3)
V(5)-O(6)	1.933(3)
V(5)-O(8)	1.933(3)
V(5)-O(3)#1	1.943(3)

V(5)-O(17)#1	1.960(3)
V(6)-O(14)	1.627(3)
V(6)-O(17)	1.931(3)
V(6)-O(13)	1.938(3)
V(6)-O(6)#1	1.952(3)
V(6)-O(16)	1.994(3)
B(1)-O(27)	1.341(5)
B(1)-O(28)	1.374(6)
B(1)-O(29)	1.377(5)
B(2)-O(26)	1.427(5)
B(2)-O(27)	1.474(5)
B(2)-O(1)	1.476(5)
B(2)-O(12)#1	1.519(5)
B(3)-O(26)	1.430(5)
B(3)-O(3)	1.468(5)
B(3)-O(24)	1.488(5)
B(3)-O(25)	1.516(5)
B(4)-O(24)	1.360(6)
B(4)-O(22)	1.356(6)
B(4)-O(23)	1.376(6)
B(5)-O(18)	1.428(5)
B(5)-O(22)	1.475(5)
B(5)-O(17)	1.478(5)
B(5)-O(25)	1.524(5)
B(6)-O(18)	1.423(5)
B(6)-O(19)	1.481(5)
B(6)-O(5)	1.480(5)
B(6)-O(16)	1.522(5)
B(7)-O(20)	1.352(6)
B(7)-O(19)	1.357(6)
B(7)-O(21)	1.380(6)
B(8)-O(11)	1.435(5)
B(8)-O(20)	1.474(5)
B(8)-O(10)	1.484(5)
B(8)-O(16)	1.512(5)
B(9)-O(11)	1.429(5)
B(9)-O(13)	1.474(5)
B(9)-O(28)#1	1.500(5)
B(9)-O(12)	1.508(5)
O(21)-H(21)	0.8400
O(23)-H(23)	0.7924
O(29)-H(29)	0.8400
C(1B)-C(2)	1.405(12)
C(1B)-N(1B)	1.501(14)

C(1B)-H(1B4)	0.9900
C(1B)-H(1B5)	0.9900
C(2)-N(2)	1.487(6)
C(2)-H(2D)	0.9900
C(2)-H(2E)	0.9900
C(3)-C(4)	1.428(10)
C(3)-N(3)	1.599(10)
C(3)-H(3D)	0.9900
C(3)-H(3E)	0.9900
C(4)-N(4)	1.476(10)
C(4)-H(4D)	0.9900
C(4)-H(4E)	0.9900
N(1B)-H(1B1)	0.9100
N(1B)-H(1B2)	0.9100
N(1B)-H(1B3)	0.9100
N(2)-H(2A)	0.9100
N(2)-H(2B)	0.9100
N(2)-H(2C)	0.9100
N(3)-H(3A)	0.9100
N(3)-H(3B)	0.9100
N(3)-H(3C)	0.9100
N(4)-H(4A)	0.9100
N(4)-H(4B)	0.9100
N(4)-H(4C)	0.9100

Table S1. Bond angles [deg] for **1**.

O(2)-V(1)-O(31)	108.28(14)
O(2)-V(1)-O(6)	106.92(14)
O(31)-V(1)-O(6)	93.55(12)
O(2)-V(1)-O(1)	108.87(14)
O(31)-V(1)-O(1)	77.66(11)
O(6)-V(1)-O(1)	144.12(12)
O(2)-V(1)-O(13)#1	106.78(14)
O(31)-V(1)-O(13)#1	144.80(12)
O(6)-V(1)-O(13)#1	79.10(12)
O(1)-V(1)-O(13)#1	88.32(12)
O(4)-V(2)-O(5)	109.49(14)
O(4)-V(2)-O(1)	109.89(14)
O(5)-V(2)-O(1)	138.28(12)
O(4)-V(2)-O(31)	107.56(14)
O(5)-V(2)-O(31)	77.84(11)

O(1)-V(2)-O(31)	77.71(12)
O(4)-V(2)-O(25)	107.32(14)
O(5)-V(2)-O(25)	90.63(11)
O(1)-V(2)-O(25)	90.51(11)
O(31)-V(2)-O(25)	145.11(12)
O(9)-V(3)-O(8)	108.00(14)
O(9)-V(3)-O(31)	106.47(14)
O(8)-V(3)-O(31)	94.23(12)
O(9)-V(3)-O(5)	108.02(14)
O(8)-V(3)-O(5)	143.91(12)
O(31)-V(3)-O(5)	77.65(11)
O(9)-V(3)-O(10)	106.44(14)
O(8)-V(3)-O(10)	78.39(11)
O(31)-V(3)-O(10)	146.95(12)
O(5)-V(3)-O(10)	89.47(12)
O(30)-V(4)-O(3)	109.86(14)
O(30)-V(4)-O(8)#1	108.69(14)
O(3)-V(4)-O(8)#1	78.28(12)
O(30)-V(4)-O(10)#1	107.17(14)
O(3)-V(4)-O(10)#1	140.72(12)
O(8)#1-V(4)-O(10)#1	77.93(11)
O(30)-V(4)-O(12)#1	106.31(14)
O(3)-V(4)-O(12)#1	89.86(11)
O(8)#1-V(4)-O(12)#1	145.00(12)
O(10)#1-V(4)-O(12)#1	92.04(11)
O(7)-V(5)-O(6)	106.81(15)
O(7)-V(5)-O(8)	108.09(15)
O(6)-V(5)-O(8)	92.21(12)
O(7)-V(5)-O(3)#1	111.24(15)
O(6)-V(5)-O(3)#1	141.87(12)
O(8)-V(5)-O(3)#1	78.45(12)
O(7)-V(5)-O(17)#1	108.09(15)
O(6)-V(5)-O(17)#1	78.07(12)
O(8)-V(5)-O(17)#1	143.82(12)
O(3)#1-V(5)-O(17)#1	87.94(12)
O(14)-V(6)-O(17)	107.97(14)
O(14)-V(6)-O(13)	108.46(14)
O(17)-V(6)-O(13)	141.26(12)
O(14)-V(6)-O(6)#1	107.42(14)
O(17)-V(6)-O(6)#1	78.33(12)
O(13)-V(6)-O(6)#1	78.64(12)
O(14)-V(6)-O(16)	107.49(14)
O(17)-V(6)-O(16)	91.26(12)
O(13)-V(6)-O(16)	90.13(12)

O(6)#1-V(6)-O(16)	145.08(12)
O(27)-B(1)-O(28)	122.4(4)
O(27)-B(1)-O(29)	117.7(4)
O(28)-B(1)-O(29)	119.9(4)
O(26)-B(2)-O(27)	107.6(3)
O(26)-B(2)-O(1)	111.1(3)
O(27)-B(2)-O(1)	108.5(3)
O(26)-B(2)-O(12)#1	112.6(3)
O(27)-B(2)-O(12)#1	109.2(3)
O(1)-B(2)-O(12)#1	107.7(3)
O(26)-B(3)-O(3)	110.3(3)
O(26)-B(3)-O(24)	107.4(3)
O(3)-B(3)-O(24)	109.0(3)
O(26)-B(3)-O(25)	112.6(3)
O(3)-B(3)-O(25)	108.0(3)
O(24)-B(3)-O(25)	109.5(3)
O(24)-B(4)-O(22)	122.7(4)
O(24)-B(4)-O(23)	116.9(4)
O(22)-B(4)-O(23)	120.4(4)
O(18)-B(5)-O(22)	107.6(3)
O(18)-B(5)-O(17)	110.7(3)
O(22)-B(5)-O(17)	109.2(3)
O(18)-B(5)-O(25)	113.4(3)
O(22)-B(5)-O(25)	108.3(3)
O(17)-B(5)-O(25)	107.6(3)
O(18)-B(6)-O(19)	107.0(3)
O(18)-B(6)-O(5)	111.7(3)
O(19)-B(6)-O(5)	108.7(3)
O(18)-B(6)-O(16)	112.9(3)
O(19)-B(6)-O(16)	109.9(3)
O(5)-B(6)-O(16)	106.5(3)
O(20)-B(7)-O(19)	121.9(4)
O(20)-B(7)-O(21)	120.9(4)
O(19)-B(7)-O(21)	117.2(4)
O(11)-B(8)-O(20)	106.4(3)
O(11)-B(8)-O(10)	110.1(3)
O(20)-B(8)-O(10)	109.7(3)
O(11)-B(8)-O(16)	114.3(3)
O(20)-B(8)-O(16)	107.6(3)
O(10)-B(8)-O(16)	108.6(3)
O(11)-B(9)-O(13)	111.1(3)
O(11)-B(9)-O(28)#1	108.1(3)
O(13)-B(9)-O(28)#1	107.8(3)
O(11)-B(9)-O(12)	113.0(3)

O(13)-B(9)-O(12)	108.4(3)
O(28)#1-B(9)-O(12)	108.3(3)
B(2)-O(1)-V(2)	129.9(2)
B(2)-O(1)-V(1)	128.4(2)
V(2)-O(1)-V(1)	101.76(13)
B(3)-O(3)-V(4)	130.7(2)
B(3)-O(3)-V(5)#1	127.7(2)
V(4)-O(3)-V(5)#1	101.45(13)
B(6)-O(5)-V(2)	130.0(2)
B(6)-O(5)-V(3)	128.1(2)
V(2)-O(5)-V(3)	101.89(12)
V(1)-O(6)-V(5)	146.75(16)
V(1)-O(6)-V(6)#1	101.30(13)
V(5)-O(6)-V(6)#1	101.79(13)
V(3)-O(8)-V(5)	145.79(16)
V(3)-O(8)-V(4)#1	102.71(12)
V(5)-O(8)-V(4)#1	101.24(13)
B(8)-O(10)-V(4)#1	129.4(2)
B(8)-O(10)-V(3)	128.6(2)
V(4)#1-O(10)-V(3)	100.95(12)
B(9)-O(11)-B(8)	120.4(3)
B(9)-O(12)-B(2)#1	114.5(3)
B(9)-O(12)-V(4)#1	121.2(2)
B(2)#1-O(12)-V(4)#1	121.4(2)
B(9)-O(13)-V(6)	130.9(2)
B(9)-O(13)-V(1)#1	128.4(2)
V(6)-O(13)-V(1)#1	100.73(12)
B(8)-O(16)-B(6)	114.5(3)
B(8)-O(16)-V(6)	122.5(2)
B(6)-O(16)-V(6)	121.3(2)
B(5)-O(17)-V(6)	129.7(2)
B(5)-O(17)-V(5)#1	128.7(2)
V(6)-O(17)-V(5)#1	101.59(13)
B(6)-O(18)-B(5)	120.2(3)
B(7)-O(19)-B(6)	122.1(3)
B(7)-O(20)-B(8)	123.0(3)
B(7)-O(21)-H(21)	109.5
B(4)-O(22)-B(5)	122.2(3)
B(4)-O(23)-H(23)	111.1
B(4)-O(24)-B(3)	121.3(3)
B(3)-O(25)-B(5)	113.7(3)
B(3)-O(25)-V(2)	121.7(2)
B(5)-O(25)-V(2)	121.7(2)
B(2)-O(26)-B(3)	120.2(3)

B(1)-O(27)-B(2)	122.0(3)
B(1)-O(28)-B(9)#1	121.3(3)
B(1)-O(29)-H(29)	109.5
V(1)-O(31)-V(3)	144.67(16)
V(1)-O(31)-V(2)	102.59(13)
V(3)-O(31)-V(2)	102.26(12)
C(2)-C(1B)-N(1B)	105.2(10)
C(2)-C(1B)-H(1B4)	110.7
N(1B)-C(1B)-H(1B4)	110.7
C(2)-C(1B)-H(1B5)	110.7
N(1B)-C(1B)-H(1B5)	110.7
H(1B4)-C(1B)-H(1B5)	108.8
C(1B)-C(2)-N(2)	125.3(7)
N(2)-C(2)-H(2D)	110.7
N(2)-C(2)-H(2E)	110.7
H(2D)-C(2)-H(2E)	108.8
C(4)-C(3)-N(3)	110.3(7)
C(4)-C(3)-H(3D)	109.6
N(3)-C(3)-H(3D)	109.6
C(4)-C(3)-H(3E)	109.6
N(3)-C(3)-H(3E)	109.6
H(3D)-C(3)-H(3E)	108.1
C(3)-C(4)-N(4)	104.9(7)
C(3)-C(4)-H(4D)	110.8
N(4)-C(4)-H(4D)	110.8
C(3)-C(4)-H(4E)	110.8
N(4)-C(4)-H(4E)	110.8
H(4D)-C(4)-H(4E)	108.8
C(1B)-N(1B)-H(1B1)	109.5
C(1B)-N(1B)-H(1B2)	109.5
H(1B1)-N(1B)-H(1B2)	109.5
C(1B)-N(1B)-H(1B3)	109.5
H(1B1)-N(1B)-H(1B3)	109.5
H(1B2)-N(1B)-H(1B3)	109.5
C(2)-N(2)-H(2A)	109.5
C(2)-N(2)-H(2B)	109.5
H(2A)-N(2)-H(2B)	109.5
C(2)-N(2)-H(2C)	109.5
H(2A)-N(2)-H(2C)	109.5
H(2B)-N(2)-H(2C)	109.5
C(3)-N(3)-H(3A)	109.5
C(3)-N(3)-H(3B)	109.5
H(3A)-N(3)-H(3B)	109.5
C(3)-N(3)-H(3C)	109.5

H(3A)-N(3)-H(3C)	109.5
H(3B)-N(3)-H(3C)	109.5
C(4)-N(4)-H(4A)	109.5
C(4)-N(4)-H(4B)	109.5
H(4A)-N(4)-H(4B)	109.5
C(4)-N(4)-H(4C)	109.5
H(4A)-N(4)-H(4C)	109.5
H(4B)-N(4)-H(4C)	109.5

Symmetry transformations used to generate equivalent atoms:

#1 -x+1/2,-y+3/2,-z+1