Supporting Information

Figure captions:

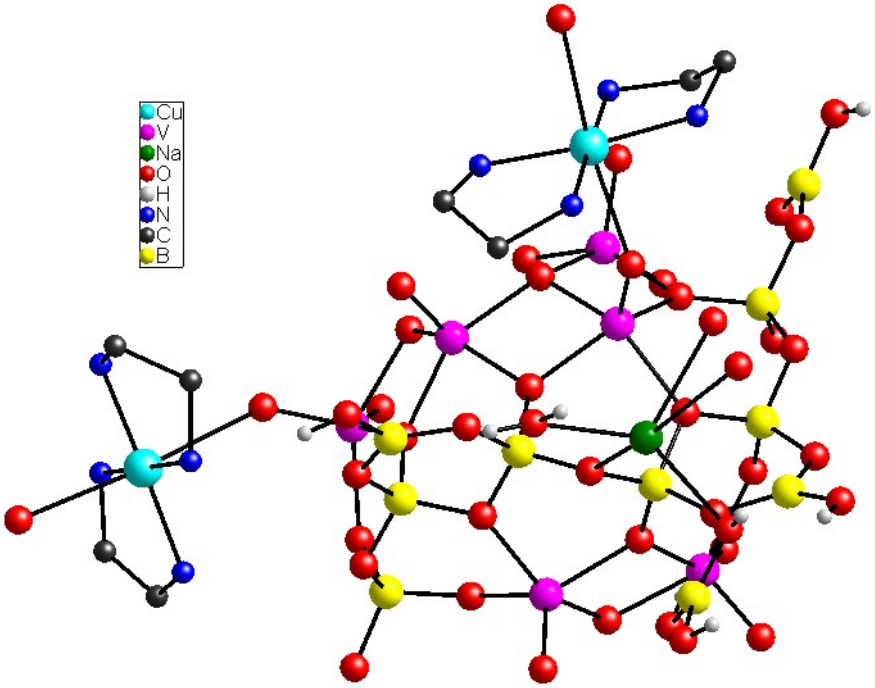

Figure S1

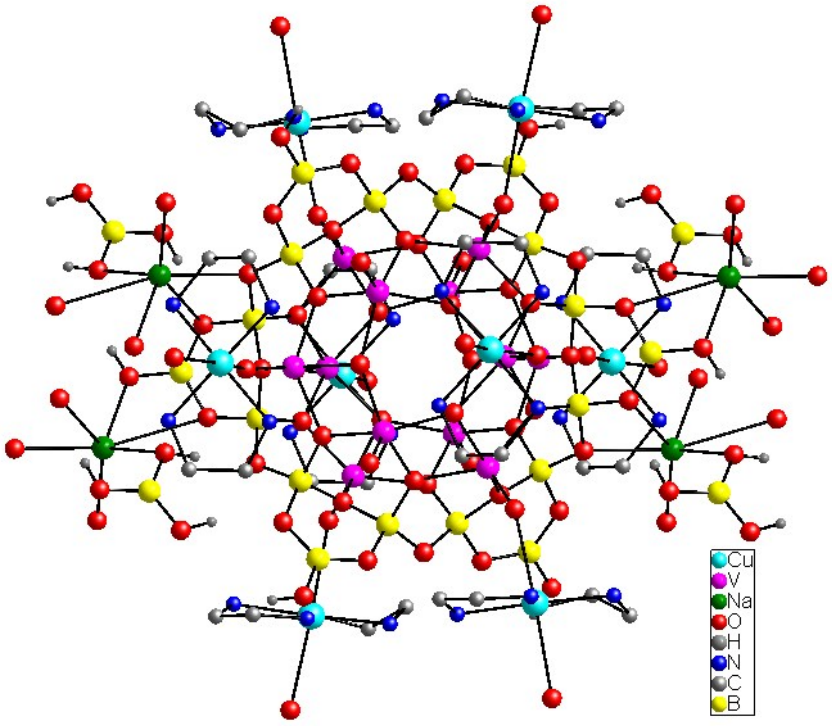

Figure S2

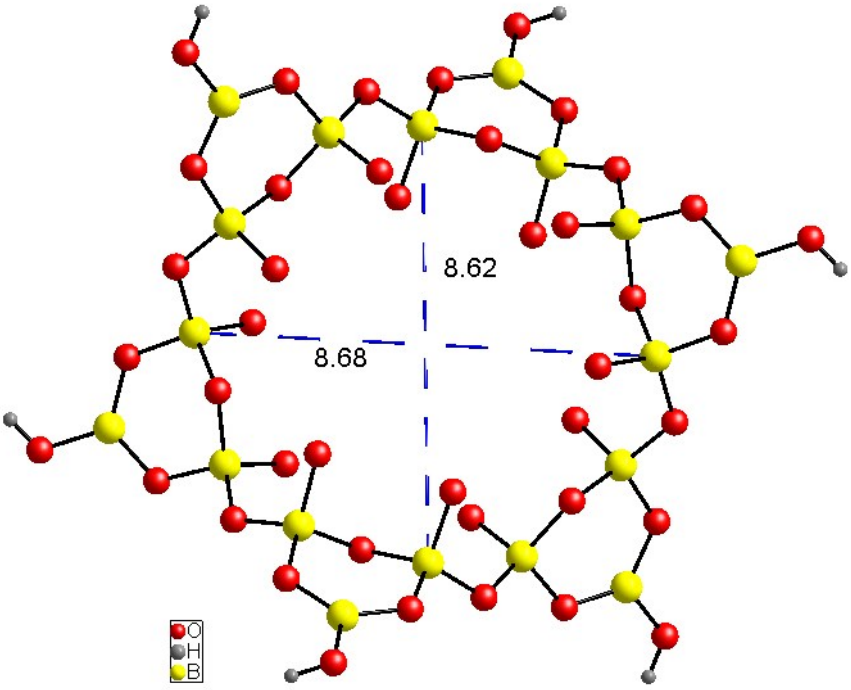

Figure S3

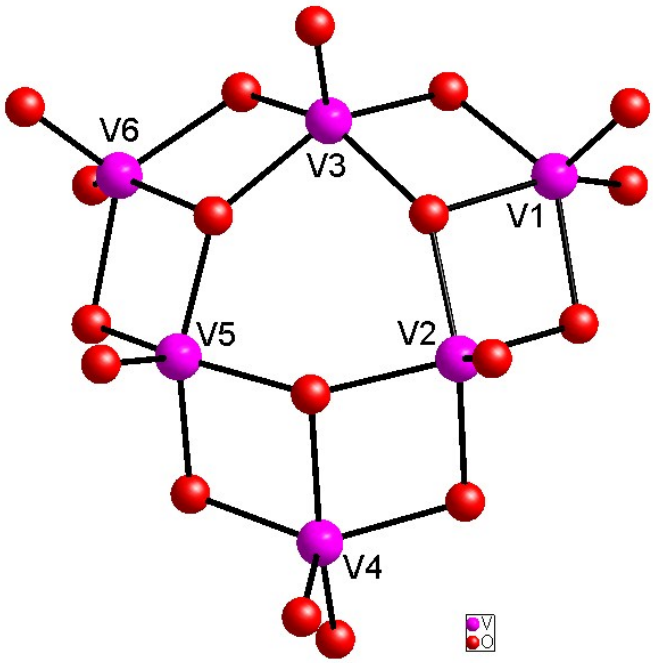

Figure S4

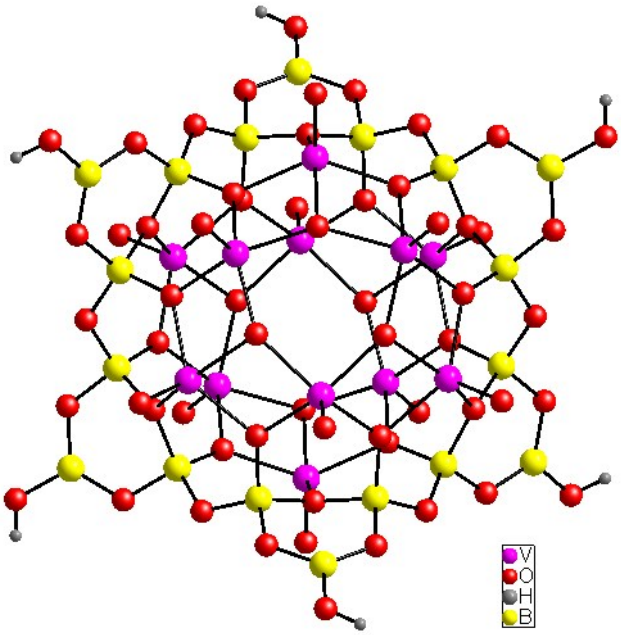

Figure S5

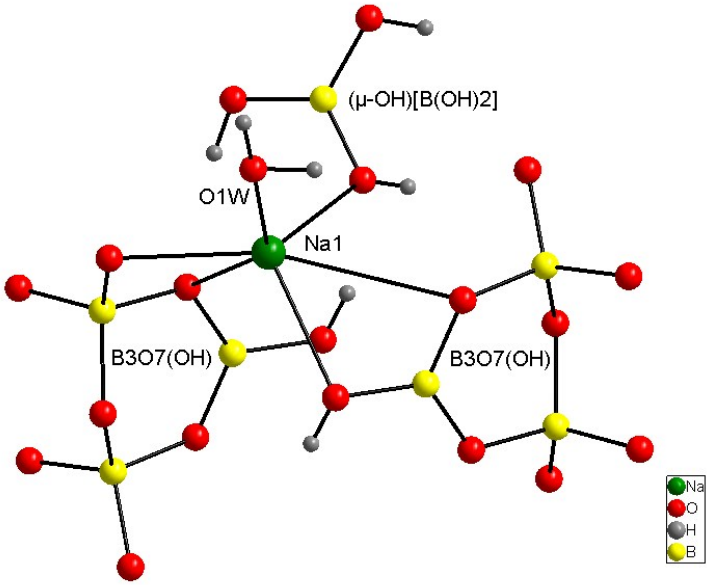

Figure S6

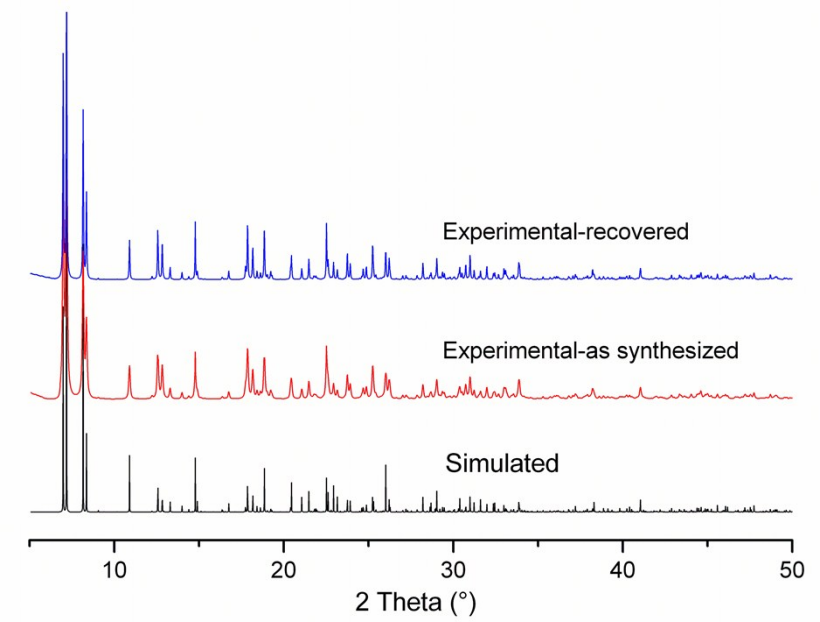

Figure S7

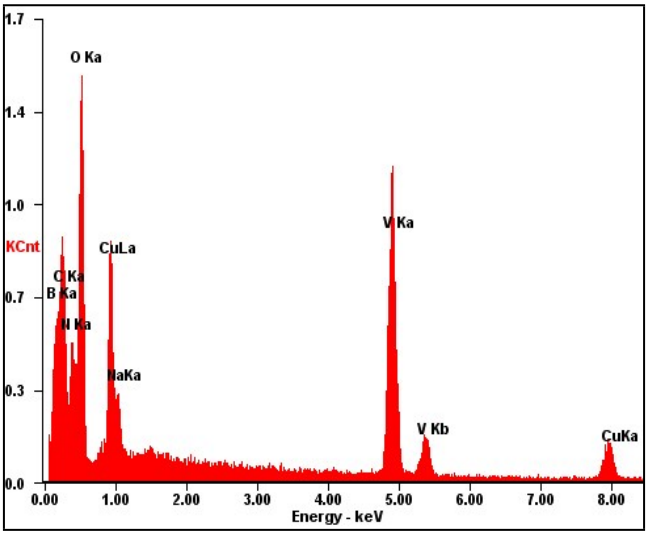

Figure S8

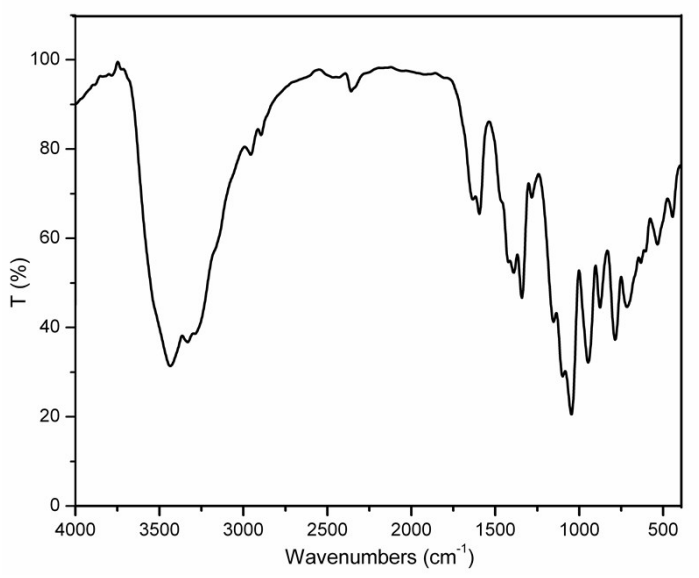

Figure S9

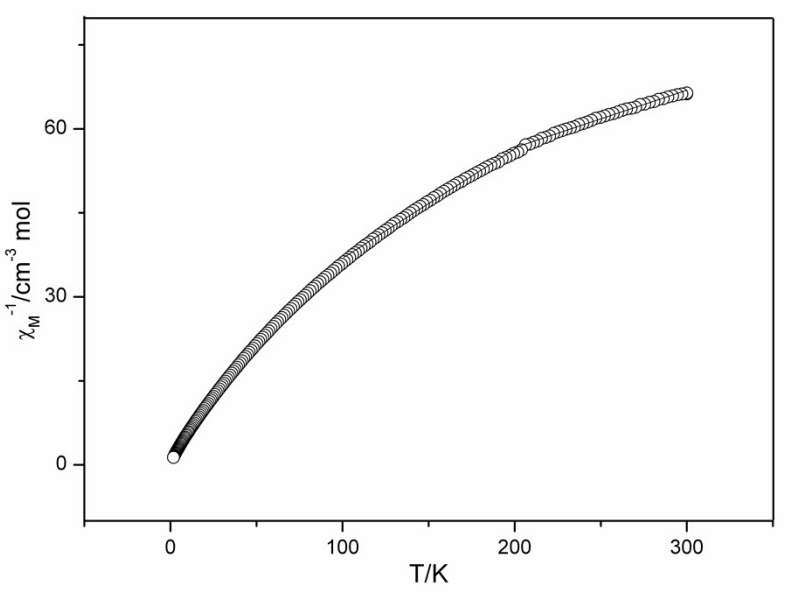

Figure S10

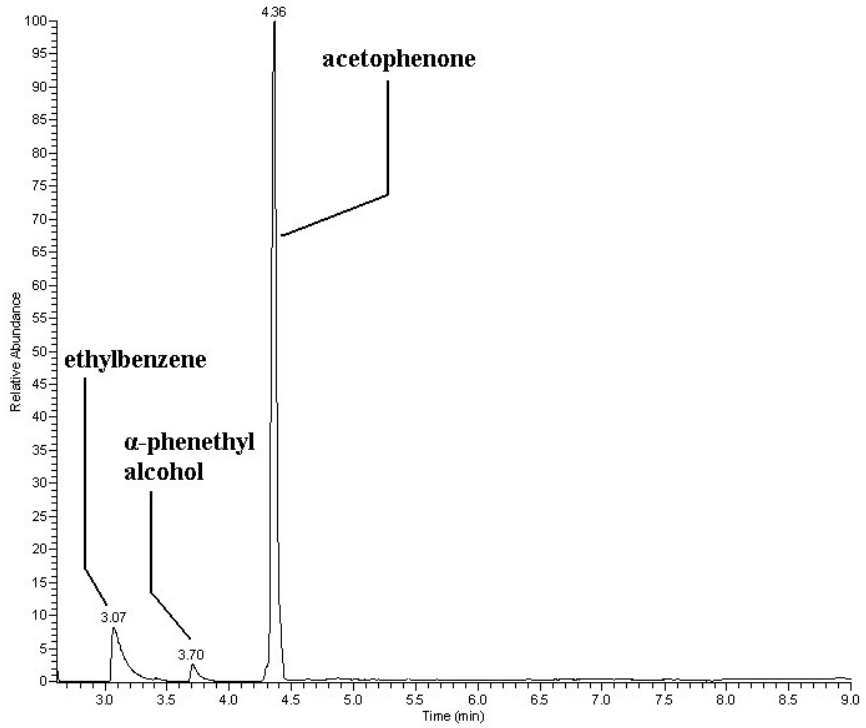

Figure S11

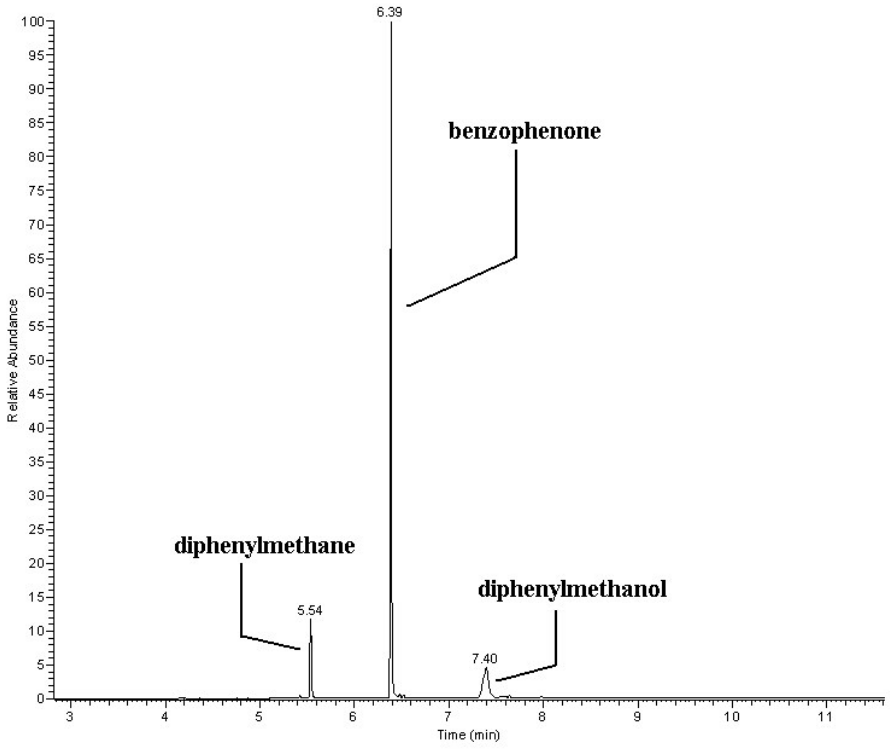

Figure S12

Table S1

Site (valence)	BVS	Site (valence)	BVS	Site (valence)	BVS
V1(+4)	4.093	Cu1(+2)	2.210	B5(+3)	3.071
V2(+4)	4.206	Cu2(+2)	2.210	B6(+3)	3.053
V3(+4)	4.371	B1(+3)	3.062	B7(+3)	3.047
V4(+4)	4.097	B2(+3)	3.110	B8(+3)	3.097
V5(+5)	4.954	B3(+3)	3.072	B9(+3)	3.084
V6(+4)	4.091	B4(+3)	3.068	B10(+3)	3.190

Table S2.

D-H	d(D-H)	d(H..A)	<DHA	d(D..A)	A	Symmetry codes
O1W-H1WA	0.869	1.910	170.38	2.770	O19	[-x+1, y+1/2, -z+3/2]
O2W-H2WA	0.829	1.995	174.11	2.821	O22	
O2W-H2WB	0.818	2.285	143.06	2.980	O4W	[x-1, -y+1/2, z+1/2]
O4-H4	0.820	1.966	150.34	2.709	O33	[x, -y+1/2, z-1/2]
O4W-H4WB	0.838	2.050	157.79	2.843	O11	[-x+1, -y, -z+1]
O19-H19	0.820	1.884	161.13	2.673	O4	[-x+1, y-1/2, -z+3/2]
O31-H31	0.674	1.945	156.87	2.578	O16	[-x+1, -y, -z+2]
O31-H31	0.674	2.630	120.13	3.025	O11	[-x+1, -y, -z+2]
O32-H32	0.820	1.981	169.81	2.792	O10	
O33-H33	0.820	1.902	162.97	2.697	O18	[-x+1, -y, -z+2]
N1-H1A	0.900	2.474	142.82	3.237	O24	
N1-H1B	0.900	2.346	129.52	3.000	O7	[-x+1, -y, -z+1]
N1-H1B	0.900	2.450	158.11	3.302	O28	[-x+1, -y, -z+1]
N2-H2A	0.900	2.245	128.84	2.896	O6W	[-x+1, -y, -z+2]

N3-H3A	0.900	2.486	126.08	3.103	O24	[-x+1, -y, -z+1]
N3-H3A	0.900	2.548	140.65	3.294	O26	[x+1, y, z]
N3-H3B	0.900	2.263	143.18	3.032	O7	
N4-H4A	0.900	2.327	163.39	3.200	O12	[-x+1, -y, -z+2]
N4-H4B	0.900	2.241	148.89	3.048	O5W	[x+1, y, z]
N5-H5A	0.900	2.244	151.52	3.065	O32	[x, -y+1/2, z-1/2]
N5-H5B	0.900	2.316	144.41	3.093	O2	
N6-H6B	0.900	2.498	146.26	3.285	O3	[x, -y+1/2, z-1/2]
N6-H6B	0.900	2.588	155.49	3.428	O22	[x, -y+1/2, z-1/2]
N7-H7A	0.900	2.409	154.60	3.245	O20	[-x, -y, -z+1]
N8-H8A	0.900	2.207	148.32	3.010	O21	[-x, y+1/2, -z+1/2]
N8-H8B	0.900	2.175	174.81	3.073	O4W	[x-1, y, z]
O12-H11	0.795	2.208	151.08	2.929	O31	
O12-H11	0.795	2.651	117.56	3.100	O15	[-x+1, -y, -z+2]

Table S3

Identification code	**NNU-6**
Empirical formula	$C_{16}H_{94}B_{20}Cu_4N_{16}Na_2O_{75}V_{12}$
Formula weight	2838.64
Temperature/K	293(2)
Crystal system	Monoclinic
Space group	$P2_1/c$ (No. 14)
a/Å	12.4021(15)
b/Å	25.291(3)
c/Å	16.5039(15)
β/°	121.510(6)
V/Å^3	4413.3(8)
Z	2
D_c/ g·cm^{-3}	2.132
μ/mm^{-1}	2.287
F(000)	2820
Reflections collected	22271
Unique data	7749
R_{int}	0.0198
Goodness-of-fit on F^2	1.037
$R_1{}^a$ [$I>2\sigma(I)$]	$R_1 = 0.0381$
$wR_2{}^b$ [all data]	$wR_2 = 0.1063$

$^aR_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $^bwR_2 = [\Sigma(w(F_o^2 - F_c^2)^2)/\Sigma(w(F_o^2)^2)]^{1/2}$.

Table S4

Bond	Distance(Å)	Bond	Distance(Å)
Cu(1)-N(3)	1.986(4)	Na(1)-O(1W)	2.218(5)
Cu(1)-N(4)	1.987(4)	Na(1)-O(8)	2.323(3)
Cu(1)-N(2)	1.994(4)	Na(1)-O(12)#4	2.352(3)
Cu(1)-N(1)	2.004(4)	Na(1)-O(31)	2.417(4)
Cu(1)-O(15)	2.436(3)	Na(1)-O(10)	2.623(3)
Cu(1)-O(27)#1	2.745(4)	Na(1)-O(11)#4	2.905(3)
Cu(2)-N(7)	1.996(4)	O(1)-B(1)	1.478(4)
Cu(2)-N(6)	2.004(4)	O(2)-B(2)	1.341(5)
Cu(2)-N(8)	2.018(4)	O(2)-B(1)	1.459(4)
Cu(2)-N(5)	2.024(3)	O(3)-B(3)	1.503(4)
Cu(2)-O(30)	2.482(3)	O(3)-B(1)	1.523(4)
Cu(2)-O(25)#2	2.480(3)	O(4)-B(2)	1.381(5)
V(1)-O(30)	1.611(2)	O(5)-B(2)	1.352(5)
V(1)-O(1)	1.928(2)	O(5)-B(3)	1.475(4)
V(1)-O(14)#3	1.933(2)	O(6)-B(3)	1.482(4)
V(1)-O(28)	1.962(2)	O(8)-B(3)	1.420(4)
V(1)-O(20)#3	2.017(2)	O(8)-B(4)	1.424(4)
V(2)-O(27)	1.606(2)	O(9)-B(4)	1.462(4)
V(2)-O(28)#3	1.927(2)	O(10)-B(5)	1.353(4)
V(2)-O(26)	1.943(2)	O(10)-B(4)	1.485(4)
V(2)-O(14)	1.952(2)	O(11)-B(5)	1.351(5)
V(2)-O(9)	1.959(2)	O(11)-B(6)	1.482(4)
V(3)-O(7)	1.601(3)	O(12)-B(5)	1.384(5)
V(3)-O(28)	1.900(2)	O(13)-B(4)	1.510(4)
V(3)-O(6)	1.929(2)	O(13)-B(6)	1.511(4)
V(3)-O(1)	1.935(2)	O(14)-B(6)	1.458(4)
V(3)-O(29)	1.938(2)	O(16)-B(7)	1.430(4)
V(4)-O(25)	1.606(2)	O(16)-B(6)	1.437(4)
V(4)-O(9)	1.928(2)	O(17)-B(7)	1.485(4)
V(4)-O(23)	1.935(2)	O(18)-B(8)	1.366(5)
V(4)-O(26)	1.986(2)	O(18)-B(7)	1.481(4)
V(4)-O(3)	2.000(2)	O(19)-B(8)	1.362(5)
V(5)-O(24)	1.590(3)	O(20)-B(7)	1.494(4)
V(5)-O(29)	1.856(2)	O(20)-B(9)#3	1.515(4)
V(5)-O(26)#3	1.865(2)	O(21)-B(8)	1.350(5)
V(5)-O(23)#3	1.915(2)	O(21)-B(9)#3	1.445(5)
V(5)-O(17)	1.922(2)	O(22)-B(1)	1.426(5)
V(6)-O(15)	1.607(3)	O(22)-B(9)	1.428(4)
V(6)-O(6)	1.922(2)	O(23)-B(9)	1.487(4)
V(6)-O(17)	1.933(2)	O(31)-B(10)	1.341(5)
V(6)-O(13)	1.988(2)	O(32)-B(10)	1.359(5)

V(6)-O(29)	2.009(2)	O(33)-B(10)	1.345(5)
Atom (1, 2, 3)	Angle(°)	Atom (1, 2, 3)	Angle(°)
V2—O26—V4	99.82(10)	O11—B6—O13	107.8(3)
V3—O28—V1	101.24(11)	O14—B6—O11	110.9(3)
V3—O29—V6	99.39(11)	O14—B6—O13	108.7(3)
V5—O29—V3	143.44(15)	O16—B6—O11	106.6(3)
V5—O29—V6	100.18(11)	O16—B6—O13	111.4(3)
O1—B1—O3	107.5(3)	O16—B6—O14	111.4(3)
O2—B1—O1	109.9(3)	O16—B7—O17	109.5(3)
O2—B1—O3	109.1(3)	O16—B7—O18	108.0(3)
O22—B1—O1	111.2(3)	O16—B7—O20	113.0(3)
O22—B1—O2	107.1(3)	O17—B7—O20	107.2(3)
O22—B1—O3	112.0(3)	O18—B7—O17	110.2(3)
O2—B2—O4	119.4(3)	O18—B7—O20	109.0(3)
O2—B2—O5	123.6(3)	B1—O1—V3	127.7(2)
O5—B2—O4	116.9(3)	O19—B8—O18	122.0(3)
O5—B3—O3	109.0(3)	O21—B8—O18	121.2(3)
O5—B3—O6	109.5(3)	O21—B8—O19	116.7(3)
O6—B3—O3	107.5(3)	B2—O2—B1	120.9(3)
O8—B3—O3	112.9(3)	O22—B9—O20i	112.3(3)
O8—B3—O5	108.3(3)	B1—O3—V4	122.0(2)
O8—B3—O6	109.7(3)	B3—O3—V4	120.9(2)
O8—B4—O9	112.3(3)	O22—B9—O23	109.9(3)
O8—B4—O10	105.1(3)	B3—O3—B1	113.2(3)
O8—B4—O13	112.8(3)	O31—B10—O32	118.3(4)
O9—B4—O10	111.3(3)	B2—O5—B3	121.3(3)
O9—B4—O13	107.8(3)	O31—B10—O33	123.2(4)
O10—B4—O13	107.5(3)	V6—O6—V3	102.89(11)
O10—B5—O12	121.1(3)	B3—O6—V3	127.0(2)
O11—B5—O10	123.0(3)	B3—O6—V6	129.5(2)
O11—B5—O12	115.8(3)	O33—B10—O32	118.5(4)

Symmetry codes: #1 x+1, y, z; #2 x,-y+1/2,z-1/2; #3 -x,-y,-z+1; #4 -x+1,-y,-z+2.