Electronic Supplementary Information for Dalton Transactions

Supporting information

Chelated orthoborate ionic liquid as a reactant for the synthesis of a new cobalt borophosphate containing extra-large 16-ring channels

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Table S1 Crystallographic data and refinement results of $(NH_4)_7Co_4(H_2O)[B_2P_4O_{15}(OH)_2]_2[H_2PO_4][HPO_4]$. [a]

Empirical formula	$H_{37}B_4Co_4N_7O_{43}P_{10}$
Formula weight	1412.03
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Orthorhombic, *Pnma* (No.62)
Unit cell dimensions	a = 16.9206(7) Å
	b = 10.5592(5) Å
	c = 21.9997(10) Å
Volume	3930.6(3) Å^3
Z, Calculated density	4, 2.386 g/cm^3
Absorption coefficient	2.211 mm^{-1}
F(000)	2832
Crystal size	0.25 × 0.10 × 0.08 mm^3
Theta range for data collection	2.14 to 28º
Limiting indices	$-22 \le h \le 22$, $-13 \le k \le 10$, $-26 \le l \le 29$
Reflections collected / unique	25209 / 4935 [R(int) = 0.0346]
Completeness to theta = 28.00	98.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.8430 and 0.6079
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4935 / 70 / 416
Goodness-of-fit on F^2	1.039
Final R indices [I>2sigma(I)]	R_1 = 0.0293, wR_2 = 0.0783
R indices (all data)	R_1 = 0.0344, wR_2 = 0.0808
Extinction coefficient	0.00037(9)
Largest diff. peak and hole	1.197 and -0.482 e Å^{-3}

[a] $R_1 = \sum(\Delta F/\sum(F_o))$; $wR_2 = (\sum[w(F_o^2-F_c^2)])/\sum[w(F_o^2)^2]^{1/2}$, $w = 1/\sigma^2(F_o^2)$

Table S2 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $(NH_4)_7Co_4(H_2O)[B_2P_4O_{15}(OH)_2]_2[H_2PO_4][HPO_4]$. [a]

	x	y	z	*U*(eq)
Co(1)	6427(1)	-2500	7597(1)	12(1)
Co(2)	7597(1)	2500	6356(1)	10(1)
Co(3)	6877(1)	2500	7673(1)	10(1)
Co(4)	6472(1)	-2500	9098(1)	14(1)
P(1)	8061(1)	-2037(1)	8283(1)	21(1)
P(2)	5104(1)	2500	5071(1)	25(1)
P(3)	6058(1)	173(1)	8406(1)	12(1)
P(4)	7202(1)	-563(1)	10220(1)	13(1)
P(5)	8833(1)	2500	7502(1)	10(1)
P(6)	6408(1)	243(1)	6734(1)	10(1)
P(7)	4534(1)	-2162(1)	9229(1)	19(1)
B(1)	6356(2)	1296(2)	5574(1)	13(1)
B(2)	5228(1)	1283(2)	7468(1)	11(1)
O(1)	5779(1)	461(2)	9073(1)	26(1)
O(2)	5348(2)	-2500	9417(1)	24(1)
O(3)	5069(2)	2500	4389(2)	48(1)
O(4)	4313(2)	-2500	8587(1)	28(1)
O(5)	5324(1)	484(2)	8018(1)	18(1)
O(6)	9372(1)	1330(1)	7658(1)	12(1)
O(7)	8061(1)	1047(2)	5834(1)	17(1)
O(8)	8118(1)	2500	7906(1)	15(1)
O(9)	7678(2)	-2500	8876(1)	24(1)
O(10)	7018(1)	1211(1)	6950(1)	12(1)
O(11)	3905(2)	-2500	9695(2)	37(1)
O(12)	5215(2)	-2500	7529(1)	32(1)
O(13)	6547(1)	2500	5852(1)	12(1)
O(14)	8073(1)	-952(2)	10087(1)	16(1)
O(15)	5572(1)	1311(2)	5291(1)	20(1)
O(16)	8940(2)	-2500	8287(1)	33(1)
O(17)	8639(1)	2500	6834(1)	15(1)
O(18)	7219(1)	918(2)	10213(1)	22(1)
O(19)	5563(1)	620(2)	6936(1)	18(1)
O(20)	6677(1)	-1001(2)	9704(1)	21(1)
O(21)	6262(1)	-1224(2)	8364(1)	15(1)
O(22)	5589(1)	2500	7559(1)	12(1)
O(23)	7644(2)	-2500	7731(1)	22(1)
O(24)	6604(1)	-1081(2)	6933(1)	17(1)
O(25)	6754(1)	1004(2)	8252(1)	24(1)
O(26)	6369(1)	250(2)	6027(1)	13(1)
O(27)	8068(2)	-517(4)	8298(2)	29(1)
O(28)	4307(2)	2500	5362(2)	47(1)

O(29)	4467(2)	-670(4)	9300(2)	33(1)
N(1)	-1548(2)	-535(2)	6889(1)	32(1)
N(2)	4400(2)	-41(4)	6011(2)	60(1)
N(3)	2760(3)	2500	5848(2)	44(1)
N(4)	-409(2)	2500	5711(2)	31(1)
N(5)	1617(2)	-2500	9176(1)	20(1)
H(1)	5860(30)	80(40)	9370(19)	80
H(122)	4960(40)	-2500	7260(30)	80
H(121)	4940(40)	-2500	7910(30)	80
H(16)	9120(40)	-2500	8640(20)	80
H(18)	6790(20)	1240(40)	10250(20)	80
H(27)	7967	0	8742	34
H(29)	5030	-446	9392	40
H(14)	-2003(15)	-880(30)	7046(16)	80
H(13)	-1270(20)	-110(30)	7190(13)	80
H(12)	-1233(19)	-1190(30)	6737(16)	80
H(11)	-1660(20)	20(30)	6577(13)	80
H(21)	3853(12)	-100(40)	6126(17)	80
H(22)	4690(20)	180(30)	6356(12)	80
H(23)	4560(20)	-800(20)	5843(15)	80
H(24)	4430(20)	620(30)	5724(14)	80
H(31)	2870(30)	2500	6269(8)	80
H(32)	3264(16)	2500	5670(20)	80
H(33)	2560(20)	1680(20)	5779(14)	80
H(43)	-470(30)	2500	5287(7)	80
H(41)	-160(20)	1750(30)	5821(15)	80
H(42)	-913(15)	2500	5880(20)	80
H(52)	1660(30)	-2500	8747(7)	80
H(53)	1880(20)	-1790(30)	9336(16)	80
H(51)	1077(11)	-2500	9280(20)	80

[a] U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table S3 Bond lengths [Å] and angles [°] for $(NH_4)_7Co_4(H_2O)[B_2P_4O_{15}(OH)_2]_2[H_2PO_4][HPO_4]$.[a]

Co(1)-O(12)	2.056(3)	Co(3)-O(25)#2	2.0400(17)
Co(1)-O(23)	2.080(3)	Co(3)-O(25)	2.0400(17)
Co(1)-O(24)#1	2.1143(17)	Co(3)-O(10)#2	2.1070(16)
Co(1)-O(24)	2.1143(17)	Co(3)-O(10)	2.1070(16)
Co(1)-O(21)	2.1777(16)	Co(3)-O(8)	2.162(2)
Co(1)-O(21)#1	2.1777(16)	Co(3)-O(22)	2.194(2)
Co(2)-O(17)	2.054(2)	Co(4)-O(2)	2.027(3)
Co(2)-O(7)	2.0705(16)	Co(4)-O(20)#1	2.0978(17)
Co(2)-O(7)#2	2.0705(17)	Co(4)-O(20)	2.0979(17)
Co(2)-O(13)	2.094(2)	Co(4)-O(9)	2.100(3)
Co(2)-O(10)	2.1267(16)	Co(4)-O(21)#1	2.1326(16)
Co(2)-O(10)#2	2.1267(16)	Co(4)-O(21)	2.1327(16)
P(1)-O(23)	1.487(3)	P(4)-O(7)#3	1.5099(17)
P(1)-O(9)	1.538(3)	P(4)-O(20)	1.5149(17)
P(1)-O(16)	1.566(3)	P(4)-O(14)	1.5571(17)
P(1)-O(27)	1.605(4)	P(4)-O(18)	1.5644(18)
P(2)-O(28)	1.493(3)	P(5)-O(8)	1.501(2)
P(2)-O(3)	1.502(4)	P(5)-O(17)	1.506(2)
P(2)-O(15)#2	1.5613(18)	P(5)-O(6)#2	1.5730(16)
P(2)-O(15)	1.5613(17)	P(5)-O(6)	1.5731(16)
P(3)-O(25)	1.5082(18)	P(6)-O(24)	1.5021(17)
P(3)-O(21)	1.5172(17)	P(6)-O(10)	1.5280(16)
P(3)-O(5)	1.5428(17)	P(6)-O(19)	1.5502(16)
P(3)-O(1)	1.5697(19)	P(6)-O(26)	1.5561(17)
P(7)-O(2)	1.480(3)	P(7)-O(11)	1.520(3)
P(7)-O(4)	1.506(3)	P(7)-O(29)	1.586(4)
B(1)-O(13)	1.447(3)	B(2)-O(22)	1.436(3)
B(1)-O(15)	1.466(3)	B(2)-O(6)#5	1.476(3)
B(1)-O(26)	1.488(3)	B(2)-O(19)	1.478(3)
B(1)-O(14)#4	1.488(3)	B(2)-O(5)	1.483(3)
O(12)-Co(1)-O(23)	176.00(12)	O(17)-Co(2)-O(7)	87.66(7)
O(12)-Co(1)-O(24)#1	95.21(8)	O(17)-Co(2)-O(7)#2	87.66(7)
O(23)-Co(1)-O(24)#1	87.61(7)	O(7)-Co(2)-O(7)#2	95.64(10)
O(12)-Co(1)-O(24)	95.21(8)	O(17)-Co(2)-O(13)	178.90(9)
O(23)-Co(1)-O(24)	87.61(7)	O(7)-Co(2)-O(13)	91.60(6)
O(24)#1-Co(1)-O(24)	90.22(9)	O(7)#2-Co(2)-O(13)	91.60(6)
O(12)-Co(1)-O(21)	85.91(8)	O(17)-Co(2)-O(10)	94.60(7)
O(23)-Co(1)-O(21)	90.95(7)	O(7)-Co(2)-O(10)	92.35(6)
O(24)#1-Co(1)-O(21)	172.93(6)	O(7)#2-Co(2)-O(10)	171.78(7)
O(24)-Co(1)-O(21)	96.63(6)	O(13)-Co(2)-O(10)	86.24(6)
O(12)-Co(1)-O(21)#1	85.91(8)	O(17)-Co(2)-O(10)#2	94.60(7)
O(23)-Co(1)-O(21)#1	90.95(7)	O(7)-Co(2)-O(10)#2	171.78(7)

O(24)#1-Co(1)-O(21)#1	96.64(6)	O(7)#2-Co(2)-O(10)#2	92.35(6)
O(24)-Co(1)-O(21)#1	172.93(6)	O(13)-Co(2)-O(10)#2	86.24(6)
O(21)-Co(1)-O(21)#1	76.46(9)	O(10)-Co(2)-O(10)#2	79.60(8)
O(25)#2-Co(3)-O(25)	101.46(12)	O(2)-Co(4)-O(20)#1	86.34(7)
O(25)#2-Co(3)-O(10)#2	89.01(7)	O(2)-Co(4)-O(20)	86.34(7)
O(25)-Co(3)-O(10)#2	169.51(7)	O(20)#1-Co(4)-O(20)	97.97(10)
O(25)#2-Co(3)-O(10)	169.50(7)	O(2)-Co(4)-O(9)	173.22(11)
O(25)-Co(3)-O(10)	89.02(7)	O(20)#1-Co(4)-O(9)	89.21(7)
O(10)#2-Co(3)-O(10)	80.50(9)	O(20)-Co(4)-O(9)	89.21(7)
O(25)#2-Co(3)-O(8)	87.16(7)	O(2)-Co(4)-O(21)#1	96.08(7)
O(25)-Co(3)-O(8)	87.16(7)	O(20)#1-Co(4)-O(21)#1	91.80(7)
O(10)#2-Co(3)-O(8)	93.98(6)	O(20)-Co(4)-O(21)#1	170.07(7)
O(10)-Co(3)-O(8)	93.98(6)	O(9)-Co(4)-O(21)#1	89.17(7)
O(25)#2-Co(3)-O(22)	88.27(6)	O(2)-Co(4)-O(21)	96.08(7)
O(25)-Co(3)-O(22)	88.27(6)	O(20)#1-Co(4)-O(21)	170.07(7)
O(10)#2-Co(3)-O(22)	91.53(6)	O(20)-Co(4)-O(21)	91.80(7)
O(10)-Co(3)-O(22)	91.53(6)	O(9)-Co(4)-O(21)	89.17(7)
O(8)-Co(3)-O(22)	172.78(9)	O(21)#1-Co(4)-O(21)	78.38(9)
O(23)-P(1)-O(9)	112.85(15)	O(28)-P(2)-O(3)	113.1(2)
O(23)-P(1)-O(16)	110.71(16)	O(28)-P(2)-O(15)#2	108.96(12)
O(9)-P(1)-O(16)	107.23(16)	O(3)-P(2)-O(15)#2	109.27(12)
O(23)-P(1)-O(27)	110.46(17)	O(28)-P(2)-O(15)	108.96(12)
O(9)-P(1)-O(27)	107.62(18)	O(3)-P(2)-O(15)	109.27(12)
O(16)-P(1)-O(27)	107.76(16)	O(15)#2-P(2)-O(15)	107.09(13)
O(25)-P(3)-O(21)	111.96(11)	O(7)#3-P(4)-O(20)	113.26(10)
O(25)-P(3)-O(5)	112.29(10)	O(7)#3-P(4)-O(14)	110.99(9)
O(21)-P(3)-O(5)	110.90(10)	O(20)-P(4)-O(14)	109.42(10)
O(25)-P(3)-O(1)	109.42(12)	O(7)#3-P(4)-O(18)	110.70(10)
O(21)-P(3)-O(1)	108.33(10)	O(20)-P(4)-O(18)	107.92(10)
O(5)-P(3)-O(1)	103.53(11)	O(14)-P(4)-O(18)	104.11(10)
O(8)-P(5)-O(17)	113.70(13)	O(24)-P(6)-O(10)	112.55(10)
O(8)-P(5)-O(6)#2	109.76(8)	O(24)-P(6)-O(19)	111.02(10)
O(17)-P(5)-O(6)#2	109.83(8)	O(10)-P(6)-O(19)	111.22(9)
O(8)-P(5)-O(6)	109.76(8)	O(24)-P(6)-O(26)	107.73(9)
O(17)-P(5)-O(6)	109.83(8)	O(10)-P(6)-O(26)	109.66(9)
O(6)#2-P(5)-O(6)	103.46(12)	O(19)-P(6)-O(26)	104.27(9)
O(2)-P(7)-O(4)	115.80(16)	O(13)-B(1)-O(15)	111.9(2)
O(2)-P(7)-O(11)	114.04(18)	O(13)-B(1)-O(26)	111.47(19)
O(4)-P(7)-O(11)	113.73(18)	O(15)-B(1)-O(26)	107.82(18)
O(2)-P(7)-O(29)	106.20(17)	O(13)-B(1)-O(14)#4	111.9(2)
O(4)-P(7)-O(29)	108.05(19)	O(15)-B(1)-O(14)#4	106.54(19)
O(11)-P(7)-O(29)	96.72(17)	O(26)-B(1)-O(14)#4	106.94(18)
O(22)-B(2)-O(6)#5	114.40(19)	O(22)-B(2)-O(5)	110.4(2)
O(22)-B(2)-O(19)	111.78(19)	O(6)#5-B(2)-O(5)	106.32(18)

O(6)#5-B(2)-O(19)	104.03(18)	O(19)-B(2)-O(5)	109.55(18)

[a]Symmetry transformations used to generate equivalent atoms: #1 x,-y-1/2,z #2 x,-y+1/2,z #3 -x+3/2,-y,z+1/2 #4 -x+3/2,-y,z-1/2 #5 x-1/2,y,-z+3/2.

Table S4 Hydrogen bonds for $(NH_4)_7Co_4(H_2O)[B_2P_4O_{15}(OH)_2]_2[H_2PO_4][HPO_4]$. [a]

D-H...A	d(D-H) [Å]	d(H...A) [Å]	d(D...A) [Å]	<(DHA) [°]
O(1)-H(1)...O(20)	0.78(4)	1.93(4)	2.573(3)	139(5)
O(12)-H(122)...O(16)#2	0.73(7)	2.10(8)	2.806(4)	162(8)
O(12)-H(121)...O(4)	0.96(7)	1.83(8)	2.782(4)	173(6)
O(16)-H(16)...O(3)#1	0.84(4)	2.14(5)	2.948(5)	161(7)
O(18)-H(18)...O(11)#3	0.81(4)	1.78(4)	2.540(3)	157(5)
O(18)-H(18)...O(29)#3	0.81(4)	2.42(4)	3.060(4)	137(4)
O(29)-H(29)...O(1)	1.00	1.74	2.569(5)	137.8
N(1)-H(14)...O(23)#4	0.920(18)	2.36(3)	3.101(3)	138(3)
N(1)-H(14)...O(24)#4	0.920(18)	2.38(3)	3.182(3)	146(3)
N(1)-H(13)...O(6)#4	0.925(18)	2.14(2)	3.028(3)	161(3)
N(1)-H(12)...O(4)#2	0.935(18)	1.808(18)	2.742(3)	176(4)
N(1)-H(12)...O(29)#2	0.935(18)	2.63(3)	3.132(5)	114(3)
N(1)-H(11)...O(7)#4	0.925(18)	2.015(18)	2.935(3)	173(3)
N(2)-H(21)...O(27)#2	0.962(18)	1.89(2)	2.765(5)	150(3)
N(2)-H(22)...O(19)	0.928(18)	2.01(2)	2.916(4)	164(3)
N(2)-H(22)...O(6)#2	0.928(18)	2.54(3)	3.267(4)	135(3)
N(2)-H(23)...O(3)#5	0.919(18)	1.973(18)	2.885(4)	171(3)
N(2)-H(23)...O(15)#5	0.919(18)	2.56(3)	3.162(4)	123(3)
N(2)-H(24)...O(28)	0.944(18)	2.15(2)	3.043(4)	158(3)
N(2)-H(24)...O(15)	0.944(18)	2.27(3)	2.912(4)	124(3)
N(3)-H(31)...O(8)#2	0.945(15)	1.861(15)	2.806(5)	179(5)
N(3)-H(32)...O(28)	0.942(15)	1.887(16)	2.827(6)	175(5)
N(3)-H(33)...O(18)#2	0.937(14)	2.40(3)	3.013(4)	123(3)
N(4)-H(43)...O(2)#6	0.937(15)	1.925(18)	2.849(5)	168(5)
N(4)-H(41)...O(1)#2	0.931(14)	2.104(19)	2.983(3)	157(3)
N(4)-H(41)...O(29)#2	0.931(14)	2.64(4)	3.354(4)	134(4)
N(4)-H(42)...O(17)#4	0.932(15)	2.23(4)	2.951(4)	134(4)
N(4)-H(42)...O(7)#4	0.932(15)	2.32(2)	3.022(4)	131.8(19)
N(4)-H(42)...O(7)#7	0.932(15)	2.32(2)	3.022(4)	131.8(19)
N(5)-H(52)...O(24)#8	0.947(15)	2.119(12)	2.861(3)	134.3(7)
N(5)-H(52)...O(24)#5	0.947(15)	2.119(12)	2.861(3)	134.3(7)
N(5)-H(53)...O(18)#3	0.944(14)	2.04(2)	2.912(3)	154(4)
N(5)-H(53)...O(26)#2	0.944(14)	2.45(4)	2.9674(17)	114(3)
N(5)-H(51)...O(3)#9	0.945(15)	1.952(16)	2.891(5)	172(4)
N(5)-H(51)...O(28)#9	0.945(15)	2.46(4)	3.042(5)	120(4)

[a]Symmetry transformations used to generate equivalent atoms: #1 -x+3/2,-y,z+1/2 #2 x-1/2,y,-z+3/2 #3 -x+1,-y,-z+2 #4 x-1,y,z #5 -x+1,-y,-z+1 #6 -x+1/2,-y,z-1/2 #7 x-1,-y+1/2,z #8 x-1/2,-y-1/2,-z+3/2 #9 -x+1/2,-y,z+1/2.

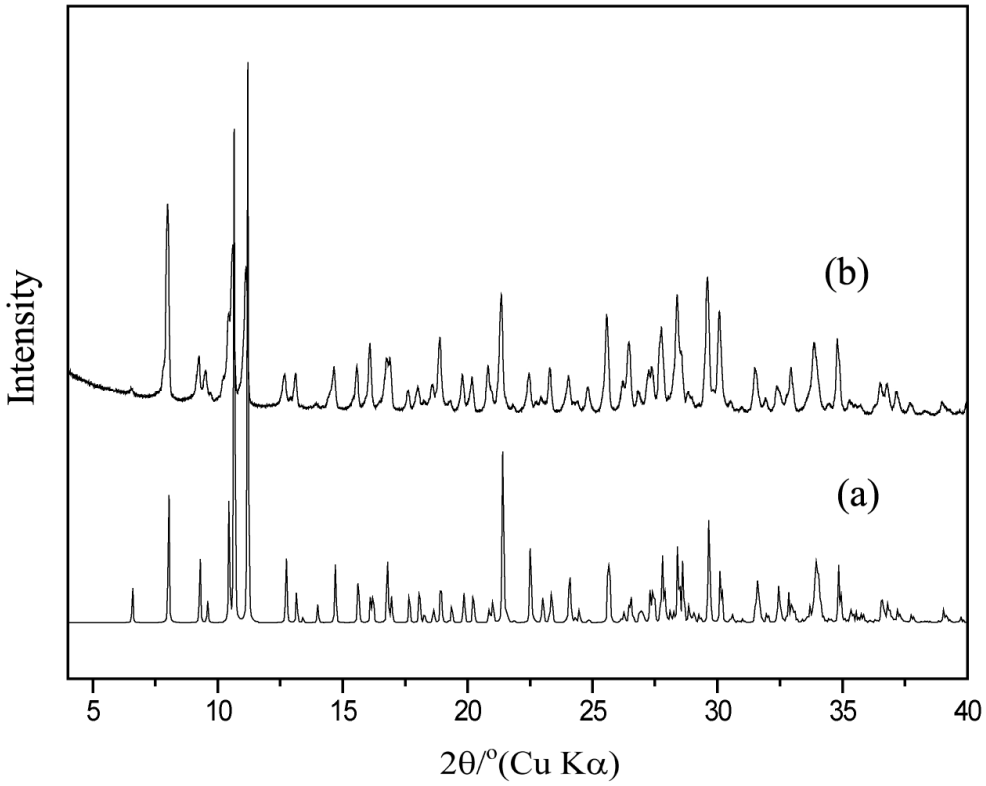

Fig. S1 Simulated (a) and experimental (b) XRD of **1**

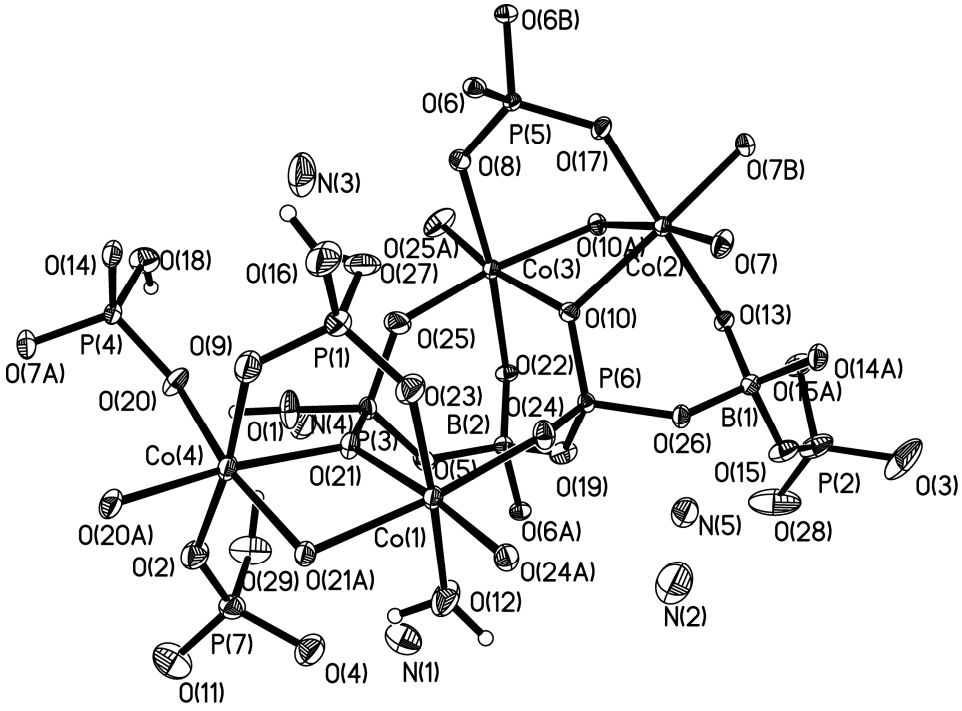

Fig. S2 Thermal ellipsoid plot (50% probability) and atomic labeling scheme of **1**

The TG-DSC measurements have been done by using a Netzsch differential scanning calorimeter (model: DSC 204), as seen in figure S3. It gives a total weight loss of 20.5 wt%. The first slight weight loss of about 0.5 wt% observed before 200 °C corresponds to the removal of physically absorbed water. A strong weight loss of about 19.4 wt % occurring from 200 to 660 °C is attributed to the removal of NH_3 molecules (calcd. 8.4 wt%) and the loss of H_2O molecules condensation from OH groups (calcd. 10.2 wt%). The remaining weight loss of about 0.6 wt % taking place after 660 °C may be due to the loss of some boron oxide which are volatile at high temperature.

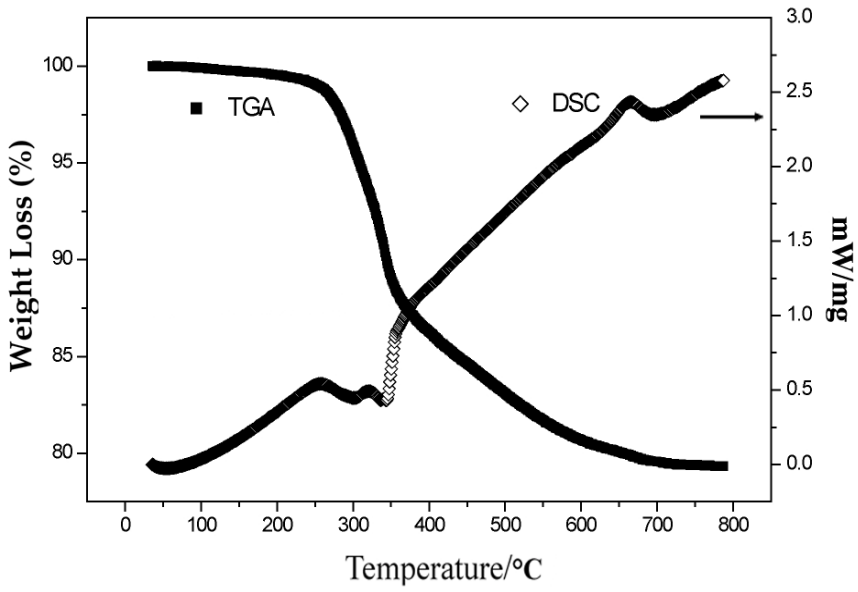

Fig. S3 TG and DSC curves of compound **1**

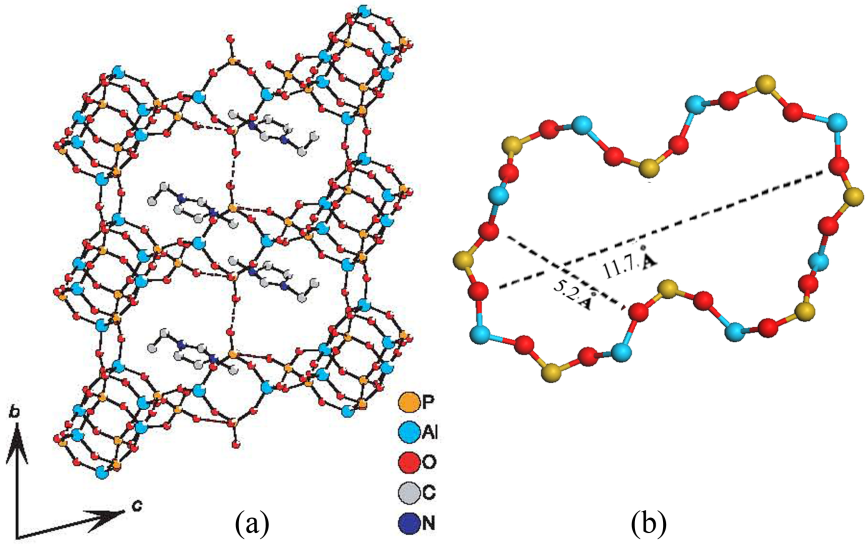

Fig. S4 The open framework of SIZ-1 (a) and the details of 16-ring channels (b)

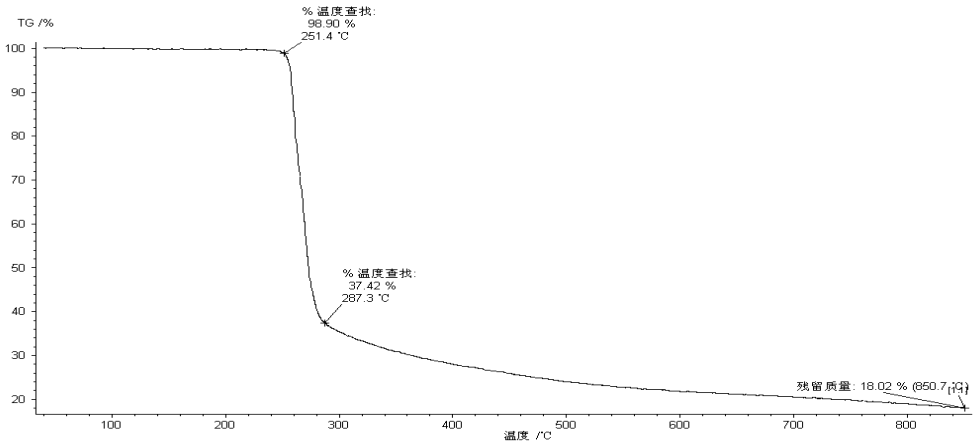

Fig. S5 TG of [Emim][BOB]

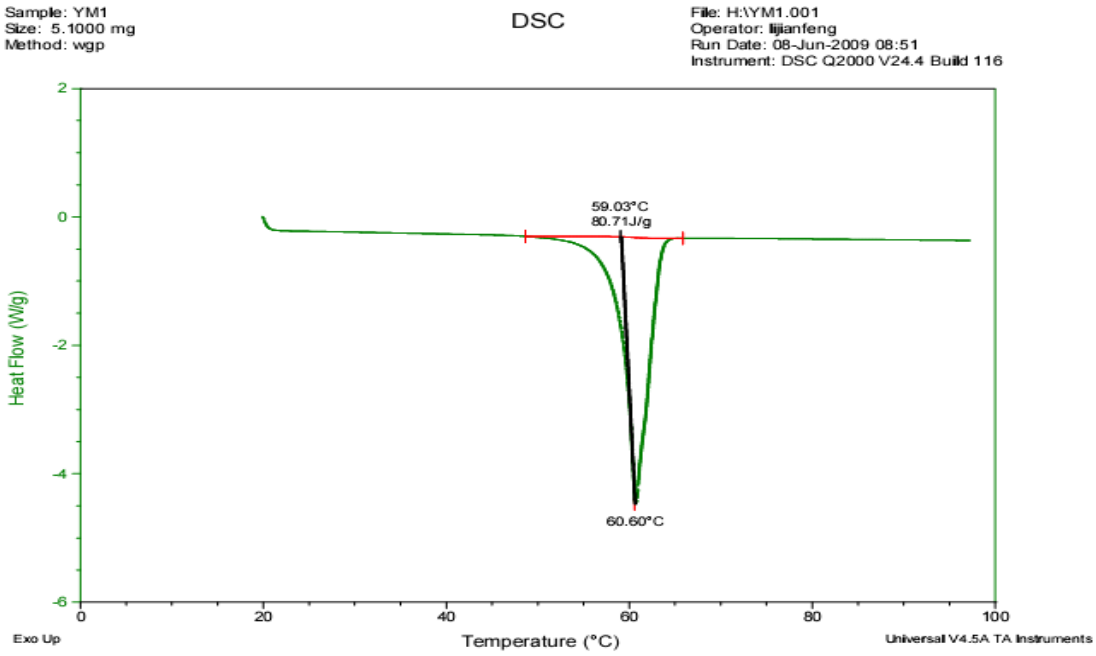

Fig. S6 DSC of [Emim][BOB]