SUPPORTING INFORMATION

Tetra-dihydrobenzoquinonate and tetra-chloranilate Zr(IV) complexes: Single-crystal-to-single-crystal phase transition and open-framework behavior for $K_4Zr(DBQ)_4$

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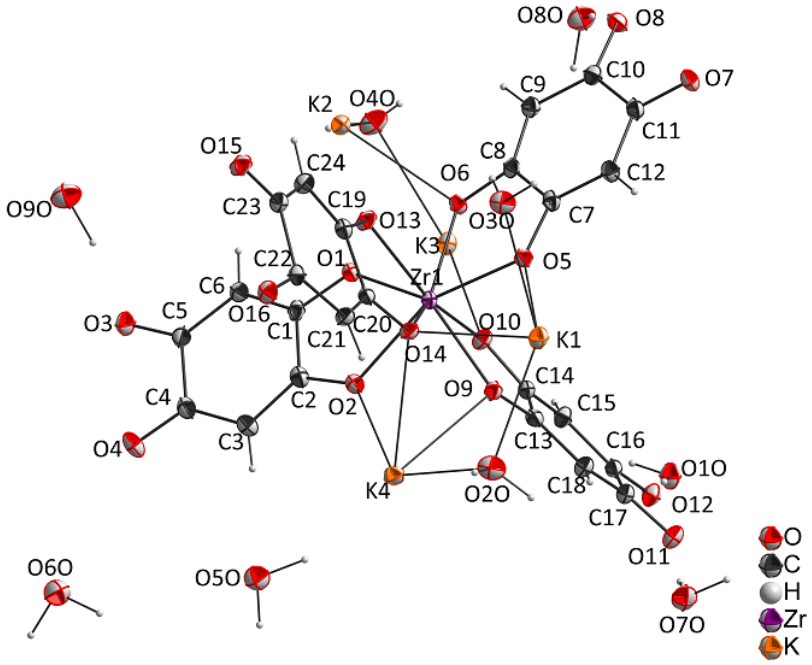
Figure S1. Ortep view of the asymmetric unit of $\{K_4[Zr(DBQ)_4]\}\cdot 9H_2O$ (**1a**) with ellipsoids cut at the 30% probability level.



Tables S1. Selected bond lengths (Å) and angles (°) for compound **1a**:

Atoms 1,2	d 1,2 (Å)	Atoms 1,2	d 1,2 (Å)
O13—C19	1.302(6)	C16—C17	1.556(8)
O13—Zr1	2.199(4)	C16—K4^{iii}	3.373(5)
O13—K2	2.898(4)	C17—O11	1.253(7)
O14—C20	1.313(6)	C17—K2^{iv}	3.516(6)
O14—Zr1	2.191(4)	O16—K1^{v}	2.756(4)
O14—K1	2.749(4)	O16—K3^{i}	2.822(4)
O14—K4	2.815(4)	O12—K4^{iii}	2.766(4)
O6—C8	1.305(6)	O12—K2^{iv}	2.940(4)
O6—Zr1	2.197(4)	O4—K3^{vi}	2.898(5)
O6—K2	2.742(4)	O4—K1^{i}	2.903(5)
O6—K3	2.852(4)	O8—K4^{ii}	2.613(4)
O10—C14	1.300(6)	O15—K3^{i}	2.879(4)
O10—Zr1	2.188(4)	O11—K2^{iv}	2.755(4)
O10—K3	2.818(4)	O11—K4^{iii}	3.224(4)
O5—C7	1.302(7)	O7—K2^{iii}	2.628(4)
O5—Zr1	2.183(4)	O7—K4^{ii}	2.896(5)
O5—K1	2.805(4)	O3—K3^{vi}	2.802(5)
O9—C13	1.281(6)	O3—K1^{i}	3.092(5)
O9—Zr1	2.218(4)	O1O—H1O	0.8910
O9—K4	2.836(4)	O1O—H2O	0.8100
O9—K1	2.985(4)	O2O—K4	2.701(5)
O1—C1	1.293(6)	O2O—K1	2.733(5)
O1—Zr1	2.234(4)	O2O—H3O	0.9570
O1—K2	2.883(4)	O2O—H4O	0.8350
O1—K3	2.964(4)	O4O—K2	2.732(5)
O2—C2	1.299(7)	O4O—K3	2.742(5)
O2—Zr1	2.180(4)	O4O—H7O	0.8710
O2—K4	2.825(4)	O4O—H8O	1.0040
C1—C6	1.376(8)	O3O—K1	2.781(5)

C1—C2	1.492(8)	O3O—H6O	0.8260
C3—C2	1.375(8)	O3O—H5O	0.8200
C3—C4	1.416(8)	O5O—H10O	1.0090
C3—H3	0.9300	O5O—H9O	0.9310
C6—C5	1.411(8)	O6O—H12O	1.0450
C6—H6	0.9300	O6O—H11B	1.0910
C5—O3	1.234(7)	O7O—H13O	0.9210
C5—C4	1.552(9)	O7O—H14O	0.9980
C4—O4	1.243(7)	O8O—H16O	0.9620
C4—K1^{i}	3.493(6)	O8O—H15O	0.9730
C8—C9	1.359(8)	O9O—H17O	1.0370
C8—C7	1.504(8)	O9O—H18O	1.0090
C8—K2	3.440(5)	Zr1—K1	3.9128(14)
C9—C10	1.415(8)	Zr1—K4	3.9247(14)
C9—H9	0.9300	Zr1—K3	3.9621(14)
C7—C12	1.358(8)	Zr1—K2	3.9727(14)
C12—C11	1.425(8)	K4—O8^{iv}	2.613(4)
C12—H12	0.9300	K4—O12^{i}	2.766(4)
C20—C21	1.356(8)	K4—O7^{iv}	2.896(5)
C20—C19	1.506(7)	K4—O11^{i}	3.224(4)
C20—K1	3.436(5)	K4—C16^{i}	3.373(5)
C19—C24	1.357(8)	K4—C10^{iv}	3.475(6)
C24—C23	1.418(8)	K4—K2^{vii}	3.9366(18)
C24—H24	0.9300	K2—O7^{i}	2.628(4)
C21—C22	1.418(7)	K2—O11^{ii}	2.755(4)
C21—H21	0.9300	K2—O12^{ii}	2.940(4)
C11—O7	1.238(7)	K2—C17^{ii}	3.516(6)
C11—C10	1.553(8)	K2—K4^{viii}	3.9365(18)
C10—O8	1.239(7)	K2—K3	4.0363(17)
C10—K4^{ii}	3.475(6)	K1—O16^{v}	2.756(4)
C18—C13	1.375(7)	K1—O4^{iii}	2.903(5)
C18—C17	1.404(7)	K1—O3^{iii}	3.092(5)
C18—H18	0.9300	K1—C4^{iii}	3.493(6)
C15—C14	1.367(8)	K1—K3^{ix}	3.7212(18)
C15—C16	1.417(8)	K3—O3^{vi}	2.802(5)
C15—H15	0.9300	K3—O16^{iii}	2.822(4)
C23—O15	1.247(7)	K3—O15^{iii}	2.879(4)
C23—C22	1.559(7)	K3—O4^{vi}	2.897(5)
C23—K3^{i}	3.497(6)	K3—C22^{iii}	3.493(5)
C13—C14	1.509(7)	K3—C23^{iii}	3.497(6)
C22—O16	1.230(7)	K3—K1^{x}	3.7212(18)
C22—K3^{i}	3.493(5)	K3—H7O	2.9351
C16—O12	1.232(7)		

Atoms 1,2,3	Angle 1,2,3 (°)	Atoms 1,2,3	Angle 1,2,3 (°)
C19—O13—Zr1	121.3(3)	O2—K4—O7^{iv}	142.71(13)
C19—O13—K2	136.5(3)	O9—K4—O7^{iv}	115.59(12)
Zr1—O13—K2	101.53(13)	O8^{iv}—K4—O11^{i}	87.10(12)
C20—O14—Zr1	121.2(3)	O2O—K4—O11^{i}	135.93(13)
C20—O14—K1	110.4(3)	O12^{i}—K4—O11^{i}	51.36(11)
Zr1—O14—K1	104.16(14)	O14—K4—O11^{i}	123.71(11)
C20—O14—K4	119.7(3)	O2—K4—O11^{i}	88.36(11)
Zr1—O14—K4	102.53(13)	O9—K4—O11^{i}	144.23(12)
K1—O14—K4	94.68(11)	O7^{iv}—K4—O11^{i}	80.64(11)
C8—O6—Zr1	120.9(3)	O8^{iv}—K4—C16^{i}	128.96(14)
C8—O6—K2	111.4(3)	O2O—K4—C16^{i}	107.08(14)
Zr1—O6—K2	106.56(14)	O12^{i}—K4—C16^{i}	20.22(12)
C8—O6—K3	118.9(3)	O14—K4—C16^{i}	94.03(12)
Zr1—O6—K3	102.61(13)	O2—K4—C16^{i}	96.06(12)
K2—O6—K3	92.33(11)	O9—K4—C16^{i}	144.98(13)
C14—O10—Zr1	121.4(3)	O7^{iv}—K4—C16^{i}	99.15(13)
C14—O10—K3	133.8(3)	O11^{i}—K4—C16^{i}	42.26(12)

Zr1—O10—K3	103.93(14)	O8^{iv}—K4—C10^{iv}	16.99(14)
C7—O5—Zr1	121.8(3)	O2O—K4—C10^{iv}	93.76(14)
C7—O5—K1	134.2(3)	O12^{i}—K4—C10^{iv}	122.24(13)
Zr1—O5—K1	102.62(14)	O14—K4—C10^{iv}	135.50(12)
C13—O9—Zr1	120.4(3)	O2—K4—C10^{iv}	102.78(13)
C13—O9—K4	119.3(3)	O9—K4—C10^{iv}	82.84(12)
Zr1—O9—K4	101.17(13)	O7^{iv}—K4—C10^{iv}	42.73(13)
C13—O9—K1	123.7(3)	O11^{i}—K4—C10^{iv}	91.53(12)
Zr1—O9—K1	96.40(13)	C16^{i}—K4—C10^{iv}	129.47(13)
K4—O9—K1	89.29(11)	O8^{iv}—K4—Zr1	96.53(10)
C1—O1—Zr1	119.5(3)	O2O—K4—Zr1	99.66(10)
C1—O1—K2	121.5(3)	O12^{i}—K4—Zr1	127.67(9)
Zr1—O1—K2	101.09(13)	O14—K4—Zr1	33.03(7)
C1—O1—K3	122.3(3)	O2—K4—Zr1	32.83(8)
Zr1—O1—K3	98.34(13)	O9—K4—Zr1	33.67(7)
K2—O1—K3	87.29(10)	O7^{iv}—K4—Zr1	148.03(9)
C2—O2—Zr1	121.5(3)	O11^{i}—K4—Zr1	119.90(8)
C2—O2—K4	134.0(3)	C16^{i}—K4—Zr1	112.49(10)
Zr1—O2—K4	102.52(14)	C10^{iv}—K4—Zr1	108.37(10)
O1—C1—C6	124.6(5)	O8^{iv}—K4—K2^{vii}	81.9(1)
O1—C1—C2	113.7(5)	O2O—K4—K2^{vii}	96.3(1)
C6—C1—C2	121.7(5)	O12^{i}—K4—K2^{vii}	48.25(9)
C2—C3—C4	118.6(5)	O14—K4—K2^{vii}	150.03(9)
C2—C3—H3	120.700	O2—K4—K2^{vii}	130.99(9)
C4—C3—H3	120.700	O9—K4—K2^{vii}	156.33(9)
C1—C6—C5	119.0(5)	O7^{iv}—K4—K2^{vii}	41.88(8)
C1—C6—H6	120.500	O11^{i}—K4—K2^{vii}	43.86(8)
C5—C6—H6	120.500	C16^{i}—K4—K2^{vii}	58.55(10)
O2—C2—C3	124.6(5)	C10^{iv}—K4—K2^{vii}	74.08(10)
O2—C2—C1	113.8(5)	Zr1—K4—K2^{vii}	163.62(4)
C3—C2—C1	121.6(5)	O7^{i}—K2—O4O	118.58(15)
O3—C5—C6	124.8(6)	O7^{i}—K2—O6	150.21(13)
O3—C5—C4	116.1(5)	O4O—K2—O6	82.32(13)
C6—C5—C4	119.1(5)	O7^{i}—K2—O11^{ii}	94.94(14)
O4—C4—C3	124.3(6)	O4O—K2—O11^{ii}	115.68(14)
O4—C4—C5	116.0(5)	O6—K2—O11^{ii}	94.00(12)
C3—C4—C5	119.6(5)	O7^{i}—K2—O1	105.83(12)
O4—C4—K1^{i}	52.2(3)	O4O—K2—O1	82.93(13)
C3—C4—K1^{i}	135.0(4)	O6—K2—O1	52.80(11)
C5—C4—K1^{i}	80.7(3)	O11^{ii}—K2—O1	141.01(12)
O6—C8—C9	124.2(5)	O7^{i}—K2—O13	93.99(12)
O6—C8—C7	113.4(4)	O4O—K2—O13	134.68(13)
C9—C8—C7	122.3(5)	O6—K2—O13	57.70(11)
O6—C8—K2	47.9(2)	O11^{ii}—K2—O13	89.60(12)
C9—C8—K2	89.4(3)	O1—K2—O13	56.93(11)
C7—C8—K2	134.9(3)	O7^{i}—K2—O12^{ii}	85.72(12)
C8—C9—C10	119.3(5)	O4O—K2—O12^{ii}	73.61(13)
C8—C9—H9	120.400	O6—K2—O12^{ii}	122.25(12)
C10—C9—H9	120.400	O11^{ii}—K2—O12^{ii}	54.85(12)
O5—C7—C12	126.1(5)	O1—K2—O12^{ii}	156.54(12)
O5—C7—C8	113.1(5)	O13—K2—O12^{ii}	144.17(12)
C12—C7—C8	120.8(5)	O7^{i}—K2—C8	155.41(14)
C7—C12—C11	119.6(5)	O4O—K2—C8	85.94(14)
C7—C12—H12	120.200	O6—K2—C8	20.69(12)
C11—C12—H12	120.200	O11^{ii}—K2—C8	74.17(13)
O14—C20—C21	124.6(5)	O1—K2—C8	73.41(12)
O14—C20—C19	112.9(4)	O13—K2—C8	64.52(12)
C21—C20—C19	122.5(5)	O12^{ii}—K2—C8	104.53(12)
O14—C20—K1	48.6(2)	O7^{i}—K2—C17^{ii}	104.03(14)
C21—C20—K1	97.3(3)	O4O—K2—C17^{ii}	97.31(14)
C19—C20—K1	122.2(3)	O6—K2—C17^{ii}	93.08(12)
O13—C19—C24	126.0(5)	O11^{ii}—K2—C17^{ii}	18.41(12)
O13—C19—C20	113.4(4)	O1—K2—C17^{ii}	145.69(12)

C24—C19—C20	120.6(5)	O13—K2—C17^{ii}	104.66(13)
C19—C24—C23	119.5(5)	O12^{ii}—K2—C17^{ii}	41.79(12)
C19—C24—H24	120.300	C8—K2—C17^{ii}	72.40(13)
C23—C24—H24	120.300	O7^{i}—K2—K4^{viii}	47.36(10)
C20—C21—C22	119.1(5)	O4O—K2—K4^{viii}	111.84(11)
C20—C21—H21	120.400	O6—K2—K4^{viii}	148.09(9)
C22—C21—H21	120.400	O11^{ii}—K2—K4^{viii}	54.19(9)
O7—C11—C12	124.1(6)	O1—K2—K4^{viii}	152.88(8)
O7—C11—C10	116.8(5)	O13—K2—K4^{viii}	113.43(8)
C12—C11—C10	119.1(5)	O12^{ii}—K2—K4^{viii}	44.57(8)
O8—C10—C9	124.0(6)	C8—K2—K4^{viii}	128.27(10)
O8—C10—C11	117.1(5)	C17^{ii}—K2—K4^{viii}	57.80(9)
C9—C10—C11	118.8(5)	O7^{i}—K2—Zr1	118.46(10)
C9—C10—K4^{ii}	155.8(4)	O4O—K2—Zr1	101.87(11)
C11—C10—K4^{ii}	82.2(3)	O6—K2—Zr1	32.01(8)
C13—C18—C17	119.5(5)	O11^{ii}—K2—Zr1	107.52(10)
C13—C18—H18	120.200	O1—K2—Zr1	33.49(7)
C17—C18—H18	120.200	O13—K2—Zr1	32.84(7)
C14—C15—C16	119.4(5)	O12^{ii}—K2—Zr1	152.90(9)
C14—C15—H15	120.300	C8—K2—Zr1	48.41(9)
C16—C15—H15	120.300	C17^{ii}—K2—Zr1	115.1(1)
O15—C23—C24	124.7(5)	K4^{viii}—K2—Zr1	146.04(4)
O15—C23—C22	115.9(5)	O7^{i}—K2—K3	139.18(11)
C24—C23—C22	119.4(5)	O4O—K2—K3	42.58(10)
O15—C23—K3^{i}	50.9(3)	O6—K2—K3	44.91(8)
C24—C23—K3^{i}	143.6(4)	O11^{ii}—K2—K3	125.45(10)
C22—C23—K3^{i}	77.0(3)	O1—K2—K3	47.19(8)
O9—C13—C18	124.8(5)	O13—K2—K3	92.13(8)
O9—C13—C14	114.0(4)	O12^{ii}—K2—K3	111.26(9)
C18—C13—C14	121.2(5)	C8—K2—K3	58.07(9)
O10—C14—C15	125.8(5)	C17^{ii}—K2—K3	113.29(10)
O10—C14—C13	113.1(4)	K4^{viii}—K2—K3	154.09(4)
C15—C14—C13	121.1(5)	Zr1—K2—K3	59.29(3)
O16—C22—C21	124.6(5)	O2O—K1—O14	80.07(13)
O16—C22—C23	117.2(5)	O2O—K1—O16^{v}	70.36(13)
C21—C22—C23	118.1(5)	O14—K1—O16^{v}	108.91(12)
O16—C22—K3^{i}	48.0(3)	O2O—K1—O3O	137.27(14)
C21—C22—K3^{i}	149.8(4)	O14—K1—O3O	80.23(13)
C23—C22—K3^{i}	77.3(3)	O16^{v}—K1—O3O	80.88(13)
O12—C16—C15	125.3(5)	O2O—K1—O5	129.99(13)
O12—C16—C17	115.6(5)	O14—K1—O5	62.42(11)
C15—C16—C17	119.2(5)	O16^{v}—K1—O5	150.35(13)
O12—C16—K4^{iii}	50.9(3)	O3O—K1—O5	69.84(13)
C15—C16—K4^{iii}	131.1(4)	O2O—K1—O4^{iii}	78.50(13)
C17—C16—K4^{iii}	86.2(3)	O14—K1—O4^{iii}	138.18(13)
O11—C17—C18	125.2(5)	O16^{v}—K1—O4^{iii}	96.99(12)
O11—C17—C16	115.6(5)	O3O—K1—O4^{iii}	137.39(14)
C18—C17—C16	119.2(5)	O5—K1—O4^{iii}	107.56(12)
C18—C17—K2^{iv}	148.0(4)	O2O—K1—O9	76.70(12)
C16—C17—K2^{iv}	80.7(3)	O14—K1—O9	51.64(10)
C22—O16—K1^{v}	155.8(4)	O16^{v}—K1—O9	144.67(12)
C22—O16—K3^{i}	113.1(3)	O3O—K1—O9	117.55(12)
K1^{v}—O16—K3^{i}	83.68(11)	O5—K1—O9	54.48(11)
C16—O12—K4^{iii}	108.9(3)	O4^{iii}—K1—O9	88.49(12)
C16—O12—K2^{iv}	113.2(4)	O2O—K1—O3^{iii}	120.94(14)
K4^{iii}—O12—K2^{iv}	87.18(12)	O14—K1—O3^{iii}	158.56(12)
C4—O4—K3^{vi}	114.7(4)	O16^{v}—K1—O3^{iii}	84.27(12)
C4—O4—K1^{i}	108.0(4)	O3O—K1—O3^{iii}	85.49(13)
K3^{vi}—O4—K1^{i}	79.81(12)	O5—K1—O3^{iii}	97.66(12)
C10—O8—K4^{ii}	125.0(4)	O4^{iii}—K1—O3^{iii}	52.13(12)
C23—O15—K3^{i}	109.4(3)	O9—K1—O3^{iii}	124.70(12)
C17—O11—K2^{iv}	117.6(4)	O2O—K1—C20	85.42(14)
C17—O11—K4^{iii}	98.1(3)	O14—K1—C20	20.98(11)

K2^{iv}—O11—K4^{iii}	81.95(11)	O16^{v}—K1—C20	92.08(13)
C11—O7—K2^{iii}	131.7(4)	O3O—K1—C20	64.26(13)
C11—O7—K4^{ii}	115.6(4)	O5—K1—C20	71.38(12)
K2^{iii}—O7—K4^{ii}	90.76(13)	O4^{iii}—K1—C20	157.61(13)
C5—O3—K3^{vi}	117.8(4)	O9—K1—C20	72.58(11)
C5—O3—K1^{i}	103.5(4)	O3^{iii}—K1—C20	149.71(13)
K3^{vi}—O3—K1^{i}	78.12(12)	O2O—K1—C4^{iii}	97.54(14)
H1O—O1O—H2O	100.800	O14—K1—C4^{iii}	138.95(13)
K4—O2O—K1	97.73(15)	O16^{v}—K1—C4^{iii}	108.65(13)
K4—O2O—H3O	117.300	O3O—K1—C4^{iii}	121.77(14)
K1—O2O—H3O	105.700	O5—K1—C4^{iii}	91.23(12)
K4—O2O—H4O	111.800	O4^{iii}—K1—C4^{iii}	19.78(13)
K1—O2O—H4O	114.500	O9—K1—C4^{iii}	87.69(12)
H3O—O2O—H4O	109.300	O3^{iii}—K1—C4^{iii}	41.63(13)
K2—O4O—K3	95.04(14)	C20—K1—C4^{iii}	158.88(13)
K2—O4O—H7O	145.400	O2O—K1—K3^{ix}	77.41(10)
K3—O4O—H7O	94.100	O14—K1—K3^{ix}	152.94(9)
K2—O4O—H8O	106.100	O16^{v}—K1—K3^{ix}	48.93(9)
K3—O4O—H8O	111.100	O3O—K1—K3^{ix}	106.79(10)
H7O—O4O—H8O	101.500	O5—K1—K3^{ix}	144.64(9)
K1—O3O—H6O	110.800	O4^{iii}—K1—K3^{ix}	50.03(9)
K1—O3O—H5O	113.900	O9—K1—K3^{ix}	134.62(8)
H6O—O3O—H5O	110.200	O3^{iii}—K1—K3^{ix}	47.47(9)
H10O—O5O—H9O	109.900	C20—K1—K3^{ix}	140.71(10)
H12O—O6O—H11B	106.600	C4^{iii}—K1—K3^{ix}	59.73(10)
H13O—O7O—H14O	111.800	O2O—K1—Zr1	99.35(10)
H16O—O8O—H15O	90.700	O14—K1—Zr1	32.89(8)
H17O—O9O—H18O	96.300	O16^{v}—K1—Zr1	141.06(9)
O2—Zr1—O5	150.26(14)	O3O—K1—Zr1	83.45(10)
O2—Zr1—O10	88.29(15)	O5—K1—Zr1	32.99(8)
O5—Zr1—O10	93.96(15)	O4^{iii}—K1—Zr1	118.22(9)
O2—Zr1—O14	76.80(14)	O9—K1—Zr1	34.29(7)
O5—Zr1—O14	82.31(14)	O3^{iii}—K1—Zr1	129.72(9)
O10—Zr1—O14	139.05(14)	C20—K1—Zr1	49.09(9)
O2—Zr1—O6	138.26(14)	C4^{iii}—K1—Zr1	109.93(10)
O5—Zr1—O6	70.71(13)	K3^{ix}—K1—Zr1	168.10(4)
O10—Zr1—O6	77.53(14)	O4O—K3—O3^{vi}	112.25(15)
O14—Zr1—O6	136.75(13)	O4O—K3—O10	134.30(13)
O2—Zr1—O13	101.55(15)	O3^{vi}—K3—O10	86.62(13)
O5—Zr1—O13	91.00(15)	O4O—K3—O16^{iii}	134.46(14)
O10—Zr1—O13	150.36(14)	O3^{vi}—K3—O16^{iii}	88.67(13)
O14—Zr1—O13	70.58(13)	O10—K3—O16^{iii}	84.52(12)
O6—Zr1—O13	76.62(14)	O4O—K3—O6	80.17(13)
O2—Zr1—O9	78.68(14)	O3^{vi}—K3—O6	131.35(14)
O5—Zr1—O9	74.22(14)	O10—K3—O6	57.92(11)
O10—Zr1—O9	70.47(14)	O16^{iii}—K3—O6	116.52(11)
O14—Zr1—O9	69.29(13)	O4O—K3—O15^{iii}	87.00(14)
O6—Zr1—O9	129.98(14)	O3^{vi}—K3—O15^{iii}	140.46(14)
O13—Zr1—O9	138.64(14)	O10—K3—O15^{iii}	104.59(12)
O2—Zr1—O1	70.20(14)	O16^{iii}—K3—O15^{iii}	55.82(12)
O5—Zr1—O1	139.41(14)	O6—K3—O15^{iii}	84.38(12)
O10—Zr1—O1	80.47(14)	O4O—K3—O4^{vi}	68.86(14)
O14—Zr1—O1	127.09(14)	O3^{vi}—K3—O4^{vi}	55.14(13)
O6—Zr1—O1	68.83(13)	O10—K3—O4^{vi}	141.70(13)
O13—Zr1—O1	76.86(14)	O16^{iii}—K3—O4^{vi}	95.64(13)
O9—Zr1—O1	137.71(14)	O6—K3—O4^{vi}	146.00(13)
O2—Zr1—K1	107.39(10)	O15^{iii}—K3—O4^{vi}	106.96(12)
O5—Zr1—K1	44.4(1)	O4O—K3—O1	81.27(13)
O10—Zr1—K1	110.54(10)	O3^{vi}—K3—O1	83.39(13)
O14—Zr1—K1	42.94(10)	O10—K3—O1	59.14(11)
O6—Zr1—K1	114.35(9)	O16^{iii}—K3—O1	143.10(12)
O13—Zr1—K1	93.26(10)	O6—K3—O1	50.97(10)
O9—Zr1—K1	49.31(10)	O15^{iii}—K3—O1	135.07(12)

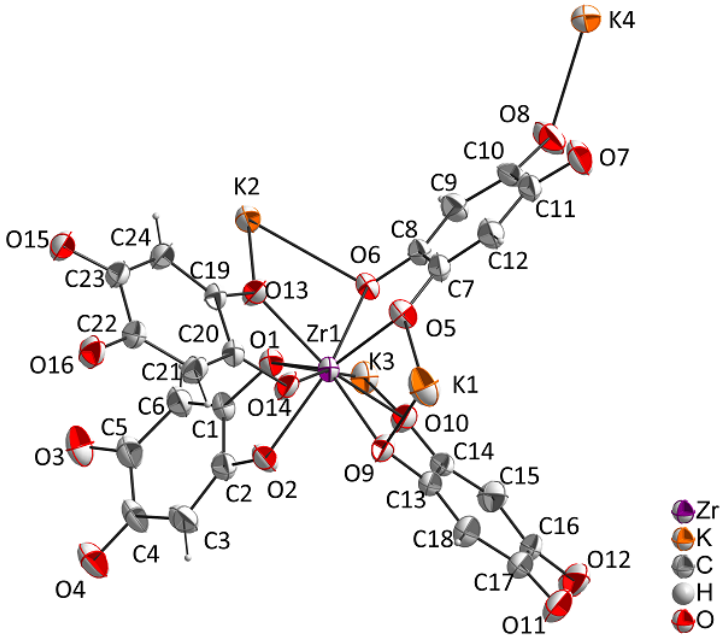
O1—Zr1—K1	168.84(10)	O4^{vi}—K3—O1	108.70(12)
O2—Zr1—K4	44.65(10)	O4O—K3—C22^{iii}	128.83(14)
O5—Zr1—K4	105.94(10)	O3^{vi}—K3—C22^{iii}	106.20(14)
O10—Zr1—K4	99.42(10)	O10—K3—C22^{iii}	78.93(12)
O14—Zr1—K4	44.44(10)	O16^{iii}—K3—C22^{iii}	18.89(12)
O6—Zr1—K4	175.13(10)	O6—K3—C22^{iii}	98.81(12)
O13—Zr1—K4	107.24(10)	O15^{iii}—K3—C22^{iii}	42.58(12)
O9—Zr1—K4	45.15(10)	O4^{vi}—K3—C22^{iii}	111.27(13)
O1—Zr1—K4	114.64(10)	O1—K3—C22^{iii}	136.63(12)
K1—Zr1—K4	62.95(3)	O4O—K3—C23^{iii}	106.01(15)
O2—Zr1—K3	99.67(11)	O3^{vi}—K3—C23^{iii}	131.40(14)
O5—Zr1—K3	102.33(10)	O10—K3—C23^{iii}	87.52(12)
O10—Zr1—K3	43.66(10)	O16^{iii}—K3—C23^{iii}	42.74(12)
O14—Zr1—K3	174.82(10)	O6—K3—C23^{iii}	83.07(12)
O6—Zr1—K3	44.63(9)	O15^{iii}—K3—C23^{iii}	19.64(12)
O13—Zr1—K3	106.77(10)	O4^{vi}—K3—C23^{iii}	118.10(13)
O9—Zr1—K3	114.01(10)	O1—K3—C23^{iii}	132.16(12)
O1—Zr1—K3	47.75(10)	C22^{iii}—K3—C23^{iii}	25.77(12)
K1—Zr1—K3	142.23(3)	O4O—K3—K1^{x}	112.99(10)
K4—Zr1—K3	134.79(3)	O3^{vi}—K3—K1^{x}	54.41(11)
O2—Zr1—K2	108.73(10)	O10—K3—K1^{x}	111.73(9)
O5—Zr1—K2	99.37(10)	O16^{iii}—K3—K1^{x}	47.39(8)
O10—Zr1—K2	104.76(10)	O6—K3—K1^{x}	163.63(9)
O14—Zr1—K2	116.11(10)	O15^{iii}—K3—K1^{x}	86.59(9)
O6—Zr1—K2	41.43(10)	O4^{vi}—K3—K1^{x}	50.16(10)
O13—Zr1—K2	45.62(10)	O1—K3—K1^{x}	137.79(8)
O9—Zr1—K2	171.38(10)	C22^{iii}—K3—K1^{x}	65.55(9)
O1—Zr1—K2	45.41(10)	C23^{iii}—K3—K1^{x}	83.84(10)
K1—Zr1—K2	129.43(3)	O4O—K3—Zr1	101.93(10)
K4—Zr1—K2	143.44(3)	O3^{vi}—K3—Zr1	100.02(12)
K3—Zr1—K2	61.15(3)	O10—K3—Zr1	32.41(8)
O8^{iv}—K4—O2O	108.20(14)	O16^{iii}—K3—Zr1	114.07(9)
O8^{iv}—K4—O12^{i}	128.96(14)	O6—K3—Zr1	32.76(7)
O2O—K4—O12^{i}	90.04(13)	O15^{iii}—K3—Zr1	109.64(9)
O8^{iv}—K4—O14	127.77(13)	O4^{vi}—K3—Zr1	141.67(9)
O2O—K4—O14	79.45(13)	O1—K3—Zr1	33.91(7)
O12^{i}—K4—O14	101.85(12)	C22^{iii}—K3—Zr1	103.25(9)
O8^{iv}—K4—O2	86.26(13)	C23^{iii}—K3—Zr1	100.22(10)
O2O—K4—O2	132.45(13)	K1^{x}—K3—Zr1	142.31(4)
O12^{i}—K4—O2	116.04(12)	O4O—K3—H7O	17.220
O14—K4—O2	57.55(11)	O3^{vi}—K3—H7O	116.01(10)
O8^{iv}—K4—O9	77.29(13)	O10—K3—H7O	147.350
O2O—K4—O9	79.80(12)	O16^{iii}—K3—H7O	117.30(9)
O12^{i}—K4—O9	153.75(12)	O15^{iii}—K3—H7O	73.580
O14—K4—O9	52.67(11)	O4^{vi}—K3—H7O	64.38(9)
O2—K4—O9	59.00(11)	O1—K3—H7O	98.410
O8^{iv}—K4—O7^{iv}	57.86(13)	C22^{iii}—K3—H7O	113.46(10)
O2O—K4—O7^{iv}	74.23(14)	C23^{iii}—K3—H7O	93.18(9)
O12^{i}—K4—O7^{iv}	84.13(12)	K1^{x}—K3—H7O	100.78(4)
O14—K4—O7^{iv}	153.03(13)	Zr1—K3—H7O	116.220

(i) 0.5+x, y, 0.5-z; (ii) 0.5-x, 0.5+y, z; (iii) -0.5+x, y, 0.5-z; (iv) 0.5-x, -0.5+y, z;
(v) 1-x, -y, -z; (vi) 1-x, -y, 1-z; (vii) 1-x, -0.5+y, 0.5-z; (viii) 1-x, 0.5+y, 0.5-z;
(ix) 0.5-x, -y, -0.5+z; (x) 0.5-x, -y, 0.5+z; (xi) -x, 0.5+y, 0.5-z; (xii) -x, -y, 1-z

- Kx···Oy and Kx···Oz distances and Oy−Kx−Oz angles for compound **1a**.

Kx	Oy	Dist (Kx···Oy) (Å)	Oz	Dist (Kx···Oz) (Å)	Angle (Oy···Kx···Oz) (°)
K4	$O8^{iv}$	2.61(2)	$O12^{i}$	2.77(2)	128.9(6)
	$O8^{iv}$	2.61(2)	O14	2.82(2)	127.8(6)
	$O8^{iv}$	2.61(2)	O2	2.82(2)	86.3(6)
	$O8^{iv}$	2.61(2)	O9	2.84(2)	77.3(6)
	$O12^{i}$	2.77(2)	O14	2.82(2)	101.8(6)
	$O12^{i}$	2.77(2)	O2	2.82(2)	116.1(6)
	$O12^{i}$	2.77(2)	O9	2.84(2)	153.8(6)
	$O12^{i}$	2.77(2)	$O7^{iv}$	2.90(2)	84.1(6)
	O14	2.82(2)	$O7^{iv}$	2.90(2)	153.0(6)
	O2	2.82(2)	$O7^{iv}$	2.90(2)	142.7(6)
	O9	2.84(2)	$O7^{iv}$	2.90(2)	115.5(6)
K2	$O7^{i}$	2.63(2)	O6	2.74(2)	150.2(6)
	$O7^{i}$	2.63(2)	$O11^{ii}$	2.76(2)	95.0(7)
	$O7^{i}$	2.63(2)	O1	2.88(2)	105.8(6)
	$O7^{i}$	2.63(2)	O13	2.90(2)	94.0(6)
	$O7^{i}$	2.63(2)	$O12^{ii}$	2.94(2)	85.7(6)
	O6	2.74(2)	$O11^{ii}$	2.76(2)	94.1(6)
	O6	2.74(2)	$O12^{ii}$	2.94(2)	122.3(6)
	$O11^{ii}$	2.76(2)	O8	2.88(2)	141.1(6)
	$O11^{ii}$	2.76(2)	O13	2.90(2)	89.6(6)
	O1	2.88(2)	$O12^{ii}$	2.94(2)	156.5(6)
	O13	2.90(2)	$O12^{ii}$	2.94(2)	144.2(6)
K1	O14	2.75(2)	$O16^{v}$	2.76(2)	108.9(6)
	O14	2.75(2)	$O4^{iii}$	2.90(2)	138.2(6)
	$O16^{v}$	2.76(2)	O5	2.81(2)	150.4(6)
	$O16^{v}$	2.76(2)	$O4^{iii}$	2.90(2)	97.0(6)
	$O16^{v}$	2.76(2)	O9	2.99(2)	144.7(6)
	O5	2.81(2)	$O4^{iii}$	2.90(2)	107.5(6)
	$O4^{iii}$	2.90(2)	O9	2.99(2)	88.5(6)
K3	$O3^{vi}$	2.80(2)	O10	2.82(2)	86.6(6)
	$O3^{vi}$	2.80(2)	$O16^{iii}$	2.82(2)	88.6(7)
	$O3^{vi}$	2.80(2)	O6	2.85(2)	131.3(6)
	$O3^{vi}$	2.80(2)	$O15^{iii}$	2.88(2)	140.5(7)
	$O3^{vi}$	2.80(2)	O1	2.97(2)	83.4(6)
	O10	2.82(2)	$O16^{iii}$	2.82(2)	84.5(6)
	O10	2.82(2)	$O15^{iii}$	2.88(2)	104.5(6)
	O10	2.82(2)	$O4^{vi}$	2.90(2)	141.7(6)
	$O16^{iii}$	2.82(20)	O6	2.85(2)	116.6(6)
	$O16^{iii}$	2.82(2)	$O15^{iii}$	2.90(2)	95.6(6)
	$O16^{iii}$	2.82(2)	O1	2.97(2)	143.1(6)
	O6	2.86(2)	$O15^{iii}$	2.88(2)	84.4(6)
	O6	2.86(2)	$O4^{vi}$	2.90(2)	146.0(6)
	O15	2.88(2)	$O4^{vi}$	2.90(2)	107.0 (6)
	O15	2.88(2)	O1	2.97(2)	135.0(6)
	O14	2.90(2)	O1	2.97(2)	108.7(6)

Figure S2. Ortep view of the asymmetric unit of $\{K_4[Zr(DBQ)_4]\}$ (**1b**) with ellipsoids cut at the 30% probability level.



Tables S2. Selected bond lengths (Å) and angles (°) for compound **1b**:

- Selected metric data for compound **1b**.

Atoms 1,2	d 1,2 (Å)	Atoms 1,2	d 1,2 (Å)
Zr1—O13	2.167(5)	C15—K1^{vi}	3.182(8)
Zr1—O5	2.174(5)	C15—H15	0.9300
Zr1—O2	2.187(5)	C8—O6	1.305(8)
Zr1—O6	2.204(4)	C8—C7	1.478(10)
Zr1—O1	2.210(5)	C23—O15	1.245(8)
Zr1—O9	2.211(4)	C23—K3^{iii}	3.426(7)
Zr1—O10	2.224(5)	C18—C17	1.432(11)
Zr1—O14	2.253(5)	C18—H18	0.9300
Zr1—K2	3.8401(17)	C17—O11	1.224(10)
Zr1—K4^{i}	3.9457(18)	C17—C16	1.512(12)
Zr1—K1	3.949(2)	C17—K2^{i}	3.497(8)
Zr1—K3	4.024(2)	C1—O1	1.316(8)
K2—O11^{ii}	2.633(7)	C1—C6	1.355(10)
K2—O7^{iii}	2.702(6)	C4—O4	1.232(9)
K2—O13	2.712(5)	C4—C5	1.528(12)
K2—O6	2.788(5)	C4—K1^{iii}	3.513(9)
K2—O1	2.895(5)	C19—O13	1.307(8)
K2—O12^{ii}	2.955(7)	C6—C5	1.417(11)
K2—O8^{iii}	3.055(8)	C6—H6	0.9300
K2—C11^{iii}	3.376(7)	C14—O10	1.276(8)
K2—C17^{ii}	3.497(8)	C11—C10	1.554(13)
K2—K4^{iii}	3.765(2)	C11—K2^{iv}	3.376(7)
K2—K3	4.466(3)	C10—O8	1.227(10)
K3—O15^{iv}	2.646(5)	C10—K4	3.458(8)
K3—O4^{v}	2.655(6)	C21—K4^{vii}	3.353(7)
K3—O1	2.789(5)	C21—H21	0.9300

K3—O16^{iv}	2.853(5)	O8—K4	2.662(6)
K3—O10	2.863(5)	O8—K2^{iv}	3.055(8)
K3—O6	3.273(5)	O9—K4^{i}	2.731(5)
K3—C1	3.368(7)	O9—K1	2.754(5)
K3—C23^{iv}	3.426(7)	O15—K3^{iii}	2.646(5)
K3—C22^{iv}	3.509(7)	O14—K4^{i}	2.912(5)
K3—K1^{vi}	4.350(3)	O14—K1	3.058(5)
C12—C7	1.366(10)	O11—K2^{i}	2.633(7)
C12—C11	1.407(11)	O2—K4^{i}	2.786(5)
C12—H12	0.9300	O4—K3^{v}	2.655(6)
C22—O16	1.253(8)	O4—K1^{iii}	2.986(7)
C22—C21	1.409(10)	O3—C5	1.239(10)
C22—C23	1.532(10)	O3—K1^{iii}	2.758(7)
C22—K4^{vii}	3.342(8)	O16—K3^{iii}	2.853(5)
C22—K3^{iii}	3.509(7)	O16—K1^{ix}	3.022(6)
C24—C19	1.361(9)	O16—K4^{vii}	3.054(6)
C24—C23	1.404(10)	O5—C7	1.308(8)
C24—H24	0.9300	O5—K1	2.747(5)
C20—O14	1.297(8)	K1—O3^{iv}	2.758(7)
C20—C21	1.353(9)	K1—O4^{iv}	2.986(7)
C20—C19	1.496(10)	K1—O16^{ix}	3.023(6)
C13—O9	1.304(8)	K1—C15^{x}	3.182(8)
C13—C18	1.361(10)	K1—C5^{iv}	3.437(8)
C13—C14	1.481(10)	K1—C4^{iv}	3.513(9)
C13—K4^{i}	3.401(7)	K1—K4^{i}	4.217(3)
C13—K1	3.485(7)	K4—O9^{ii}	2.731(5)
O7—C11	1.231(9)	K4—O12^{xi}	2.751(7)
O7—K2^{iv}	2.702(6)	K4—O2^{ii}	2.786(5)
O7—K4	3.174(6)	K4—O14^{ii}	2.912(5)
C9—C8	1.365(10)	K4—O16^{xii}	3.054(6)
C9—C10	1.401(11)	K4—C22^{xii}	3.342(8)
C9—H9	0.9300	K4—C21^{xii}	3.352(7)
C3—C2	1.340(11)	K4—C13^{ii}	3.402(7)
C3—C4	1.404(12)	K4—K2^{iv}	3.765(2)
C3—H3	0.9300	C5—K1^{iii}	3.438(8)
C2—O2	1.301(9)	Zr1—Zr1^{ii}	11.0383(13)
C2—C1	1.508(10)	Zr1—Zr1^{i}	11.0383(13)
O12—C16	1.253(9)	Zr1—Zr1^{x}	10.3154(12)
O12—K4^{viii}	2.751(7)	Zr1—Zr1^{vi}	10.3154(12)
O12—K2^{i}	2.955(7)	Zr1—Zr1^{xi}	16.4866(15)
C15—C14	1.381(10)	Zr1—Zr1^{xiii}	10.0475(13)
C15—C16	1.403(12)	Zr1—Zr1^{xiv}	10.0475(13)

Atoms 1,2,3	Angle 1,2,3 (°)	Atoms 1,2,3	Angle 1,2,3 (°)
O13—Zr1—O5	89.15(19)	C9—C8—C7	121.6(7)
O13—Zr1—O2	101.8(2)	O15—C23—C24	122.6(7)
O5—Zr1—O2	149.58(19)	O15—C23—C22	117.3(6)
O13—Zr1—O6	80.38(17)	C24—C23—C22	120.0(6)
O5—Zr1—O6	71.07(18)	O15—C23—K3^{iii}	42.5(3)
O2—Zr1—O6	138.4(2)	C24—C23—K3^{iii}	148.9(5)
O13—Zr1—O1	78.49(19)	C22—C23—K3^{iii}	80.3(4)
O5—Zr1—O1	140.51(18)	C13—C18—C17	119.7(7)
O2—Zr1—O1	69.89(18)	C13—C18—H18	120.100
O6—Zr1—O1	69.94(17)	C17—C18—H18	120.100
O13—Zr1—O9	136.04(18)	O11—C17—C18	123.3(9)
O5—Zr1—O9	76.07(18)	O11—C17—C16	118.8(8)
O2—Zr1—O9	76.43(18)	C18—C17—C16	117.9(7)
O6—Zr1—O9	129.97(18)	O11—C17—K2^{i}	37.5(5)
O1—Zr1—O9	136.60(18)	C18—C17—K2^{i}	154.3(6)
O13—Zr1—O10	153.27(18)	C16—C17—K2^{i}	84.1(4)
O5—Zr1—O10	94.15(19)	O1—C1—C6	125.6(7)
O2—Zr1—O10	88.6(2)	O1—C1—C2	113.1(6)
O6—Zr1—O10	75.69(18)	C6—C1—C2	121.3(6)

O1—Zr1—O10	82.23(17)	O1—C1—K3	53.3(3)
O9—Zr1—O10	70.15(17)	C6—C1—K3	97.2(5)
O13—Zr1—O14	69.62(17)	C2—C1—K3	117.4(4)
O5—Zr1—O14	80.82(18)	O4—C4—C3	124.7(8)
O2—Zr1—O14	76.77(19)	O4—C4—C5	116.1(8)
O6—Zr1—O14	138.91(18)	C3—C4—C5	119.0(7)
O1—Zr1—O14	127.22(18)	O4—C4—K1^{iii}	55.2(5)
O9—Zr1—O14	67.27(17)	C3—C4—K1^{iii}	139.9(5)
O10—Zr1—O14	137.09(17)	C5—C4—K1^{iii}	74.6(4)
O13—Zr1—K2	43.43(13)	O13—C19—C24	126.9(6)
O5—Zr1—K2	97.93(13)	O13—C19—C20	112.8(6)
O2—Zr1—K2	109.61(14)	C24—C19—C20	120.3(6)
O6—Zr1—K2	45.65(12)	C1—C6—C5	118.9(7)
O1—Zr1—K2	48.49(12)	C1—C6—H6	120.500
O9—Zr1—K2	173.94(13)	C5—C6—H6	120.500
O10—Zr1—K2	109.91(13)	O10—C14—C15	125.9(7)
O14—Zr1—K2	113.00(12)	O10—C14—C13	115.3(6)
O13—Zr1—K4^{i}	108.53(13)	C15—C14—C13	118.8(7)
O5—Zr1—K4^{i}	106.48(13)	O7—C11—C12	125.3(9)
O2—Zr1—K4^{i}	43.16(14)	O7—C11—C10	116.3(7)
O6—Zr1—K4^{i}	170.90(13)	C12—C11—C10	118.3(7)
O1—Zr1—K4^{i}	113.01(12)	O7—C11—K2^{iv}	47.5(4)
O9—Zr1—K4^{i}	41.84(12)	C12—C11—K2^{iv}	136.5(5)
O10—Zr1—K4^{i}	95.95(13)	C10—C11—K2^{iv}	84.1(4)
O14—Zr1—K4^{i}	46.84(12)	O8—C10—C9	125.5(9)
K2—Zr1—K4^{i}	142.89(4)	O8—C10—C11	115.6(7)
O13—Zr1—K1	101.14(15)	C9—C10—C11	118.8(7)
O5—Zr1—K1	41.92(13)	O8—C10—K4	41.3(4)
O2—Zr1—K1	107.72(14)	C9—C10—K4	143.3(6)
O6—Zr1—K1	112.61(13)	C11—C10—K4	86.8(4)
O1—Zr1—K1	177.37(13)	C20—C21—C22	119.8(6)
O9—Zr1—K1	42.40(13)	C20—C21—K4^{vii}	137.5(5)
O10—Zr1—K1	98.93(13)	C22—C21—K4^{vii}	77.4(4)
O14—Zr1—K1	50.50(13)	C20—C21—H21	120.100
K2—Zr1—K1	132.71(5)	C22—C21—H21	120.100
K4^{i}—Zr1—K1	64.57(4)	K4^{vii}—C21—H21	58.800
O13—Zr1—K3	111.46(14)	C10—O8—K4	121.0(5)
O5—Zr1—K3	114.75(13)	C10—O8—K2^{iv}	104.6(7)
O2—Zr1—K3	87.73(15)	K4—O8—K2^{iv}	82.06(18)
O6—Zr1—K3	54.35(13)	C13—O9—Zr1	120.7(4)
O1—Zr1—K3	41.62(12)	C13—O9—K4^{i}	109.8(4)
O9—Zr1—K3	112.34(12)	Zr1—O9—K4^{i}	105.47(17)
O10—Zr1—K3	43.70(13)	C13—O9—K1	113.5(4)
O14—Zr1—K3	164.20(13)	Zr1—O9—K1	104.83(18)
K2—Zr1—K3	69.17(4)	K4^{i}—O9—K1	100.48(16)
K4^{i}—Zr1—K3	121.60(4)	C1—O1—Zr1	120.7(4)
K1—Zr1—K3	140.22(4)	C1—O1—K3	104.5(4)
O11^{ii}—K2—O7^{iii}	134.2(2)	Zr1—O1—K3	106.63(17)
O11^{ii}—K2—O13	94.0(2)	C1—O1—K2	123.0(4)
O7^{iii}—K2—O13	112.35(16)	Zr1—O1—K2	96.65(17)
O11^{ii}—K2—O6	81.22(19)	K3—O1—K2	103.57(16)
O7^{iii}—K2—O6	144.00(18)	C23—O15—K3^{iii}	118.9(4)
O13—K2—O6	61.69(14)	C20—O14—Zr1	119.1(4)
O11^{ii}—K2—O1	133.19(19)	C20—O14—K4^{i}	119.5(4)
O7^{iii}—K2—O1	92.57(17)	Zr1—O14—K4^{i}	98.81(17)
O13—K2—O1	59.09(15)	C20—O14—K1	127.5(4)
O6—K2—O1	52.82(13)	Zr1—O14—K1	94.86(15)
O11^{ii}—K2—O12^{ii}	57.2(2)	K4^{i}—O14—K1	89.84(13)
O7^{iii}—K2—O12^{ii}	89.91(17)	C17—O11—K2^{i}	126.1(6)
O13—K2—O12^{ii}	151.12(18)	C19—O13—Zr1	122.6(4)
O6—K2—O12^{ii}	110.66(16)	C19—O13—K2	132.0(4)
O1—K2—O12^{ii}	141.35(19)	Zr1—O13—K2	103.24(19)
O11^{ii}—K2—O8^{iii}	91.28(19)	C2—O2—Zr1	123.3(4)

O7^{iii}—K2—O8^{iii}	53.95(18)	C2—O2—K4^{i}	132.1(4)
O13—K2—O8^{iii}	89.82(16)	Zr1—O2—K4^{i}	104.4(2)
O6—K2—O8^{iii}	149.65(17)	C4—O4—K3^{v}	154.2(6)
O1—K2—O8^{iii}	122.93(16)	C4—O4—K1^{iii}	105.0(5)
O12^{ii}—K2—O8^{iii}	88.95(19)	K3^{v}—O4—K1^{iii}	100.75(18)
O11^{ii}—K2—C11^{iii}	133.1(2)	C5—O3—K1^{iii}	113.0(6)
O7^{iii}—K2—C11^{iii}	19.64(17)	C8—O6—Zr1	119.4(4)
O13—K2—C11^{iii}	94.26(17)	C8—O6—K2	119.3(4)
O6—K2—C11^{iii}	141.56(17)	Zr1—O6—K2	99.93(16)
O1—K2—C11^{iii}	89.59(18)	C8—O6—K3	124.9(4)
O12^{ii}—K2—C11^{iii}	104.16(18)	Zr1—O6—K3	92.48(15)
O8^{iii}—K2—C11^{iii}	42.7(2)	K2—O6—K3	94.61(14)
O11^{ii}—K2—C17^{ii}	16.4(2)	C14—O10—Zr1	120.3(4)
O7^{iii}—K2—C17^{ii}	127.3(2)	C14—O10—K3	133.7(4)
O13—K2—C17^{ii}	109.5(2)	Zr1—O10—K3	103.83(17)
O6—K2—C17^{ii}	84.61(17)	C22—O16—K3^{iii}	111.4(4)
O1—K2—C17^{ii}	136.97(17)	C22—O16—K1^{ix}	127.1(4)
O12^{ii}—K2—C17^{ii}	42.11(19)	K3^{iii}—O16—K1^{ix}	95.48(16)
O8^{iii}—K2—C17^{ii}	96.44(18)	C22—O16—K4^{vii}	92.1(4)
C11^{iii}—K2—C17^{ii}	133.4(2)	K3^{iii}—O16—K4^{vii}	146.8(2)
O11^{ii}—K2—K4^{iii}	78.54(17)	K1^{ix}—O16—K4^{vii}	87.89(14)
O7^{iii}—K2—K4^{iii}	55.92(14)	C7—O5—Zr1	120.3(4)
O13—K2—K4^{iii}	132.66(12)	C7—O5—K1	131.0(4)
O6—K2—K4^{iii}	155.82(11)	Zr1—O5—K1	106.16(18)
O1—K2—K4^{iii}	148.17(11)	O5—C7—C12	124.8(7)
O12^{ii}—K2—K4^{iii}	46.42(13)	O5—C7—C8	114.2(6)
O8^{iii}—K2—K4^{iii}	44.45(12)	C12—C7—C8	120.9(7)
C11^{iii}—K2—K4^{iii}	62.37(14)	O5—K1—O9	58.83(14)
C17^{ii}—K2—K4^{iii}	72.31(15)	O5—K1—O3^{iv}	90.80(19)
O11^{ii}—K2—Zr1	101.75(17)	O9—K1—O3^{iv}	123.99(18)
O7^{iii}—K2—Zr1	121.06(14)	O5—K1—O4^{iv}	114.08(16)
O13—K2—Zr1	33.33(10)	O9—K1—O4^{iv}	93.35(17)
O6—K2—Zr1	34.42(9)	O3^{iv}—K1—O4^{iv}	54.92(19)
O1—K2—Zr1	34.86(9)	O5—K1—O16^{ix}	134.26(16)
O12^{ii}—K2—Zr1	144.95(13)	O9—K1—O16^{ix}	76.27(15)
O8^{iii}—K2—Zr1	121.58(13)	O3^{iv}—K1—O16^{ix}	124.0(2)
C11^{iii}—K2—Zr1	110.06(14)	O4^{iv}—K1—O16^{ix}	74.19(15)
C17^{ii}—K2—Zr1	111.60(16)	O5—K1—O14	58.99(14)
K4^{iii}—K2—Zr1	165.81(7)	O9—K1—O14	50.03(13)
O11^{ii}—K2—K3	116.93(15)	O3^{iv}—K1—O14	148.51(19)
O7^{iii}—K2—K3	100.52(15)	O4^{iv}—K1—O14	142.26(17)
O13—K2—K3	89.91(11)	O16^{ix}—K1—O14	86.54(14)
O6—K2—K3	46.91(11)	O5—K1—C15^{x}	149.3(2)
O1—K2—K3	37.37(10)	O9—K1—C15^{x}	141.56(19)
O12^{ii}—K2—K3	104.38(15)	O3^{iv}—K1—C15^{x}	88.9(2)
O8^{iii}—K2—K3	151.74(13)	O4^{iv}—K1—C15^{x}	90.52(19)
C11^{iii}—K2—K3	109.19(17)	O16^{ix}—K1—C15^{x}	68.10(18)
C17^{ii}—K2—K3	110.23(14)	O14—K1—C15^{x}	112.26(18)
K4^{iii}—K2—K3	135.33(6)	O5—K1—C5^{iv}	86.32(17)
Zr1—K2—K3	57.35(4)	O9—K1—C5^{iv}	106.09(18)
O15^{iv}—K3—O4^{v}	140.81(19)	O3^{iv}—K1—C5^{iv}	19.37(19)
O15^{iv}—K3—O1	122.08(16)	O4^{iv}—K1—C5^{iv}	42.15(19)
O4^{v}—K3—O1	92.32(17)	O16^{ix}—K1—C5^{iv}	116.17(19)
O15^{iv}—K3—O16^{iv}	58.80(15)	O14—K1—C5^{iv}	144.14(17)
O4^{v}—K3—O16^{iv}	82.19(17)	C15^{x}—K1—C5^{iv}	102.3(2)
O1—K3—O16^{iv}	147.28(16)	O5—K1—C13	66.37(15)
O15^{iv}—K3—O10	91.38(16)	O9—K1—C13	20.06(14)
O4^{v}—K3—O10	89.00(18)	O3^{iv}—K1—C13	107.85(19)
O1—K3—O10	62.10(14)	O4^{iv}—K1—C13	73.56(18)
O16^{iv}—K3—O10	85.48(15)	O16^{ix}—K1—C13	74.43(16)
O15^{iv}—K3—O6	74.13(14)	O14—K1—C13	70.09(15)
O4^{v}—K3—O6	132.56(17)	C15^{x}—K1—C13	142.1(2)
O1—K3—O6	48.52(13)	C5^{iv}—K1—C13	88.82(19)

O16^{iv}—K3—O6	115.20(15)	O5—K1—C4^{iv}	96.40(17)
O10—K3—O6	52.04(13)	O9—K1—C4^{iv}	91.60(17)
O15^{iv}—K3—C1	144.19(18)	O3^{iv}—K1—C4^{iv}	42.4(2)
O4^{v}—K3—C1	72.18(18)	O4^{iv}—K1—C4^{iv}	19.79(16)
O1—K3—C1	22.23(15)	O16^{ix}—K1—C4^{iv}	92.86(17)
O16^{iv}—K3—C1	145.85(17)	O14—K1—C4^{iv}	140.63(17)
O10—K3—C1	72.16(15)	C15^{x}—K1—C4^{iv}	103.83(19)
O6—K3—C1	70.68(15)	C5^{iv}—K1—C4^{iv}	25.4(2)
O15^{iv}—K3—C23^{iv}	18.55(15)	C13—K1—C4^{iv}	71.87(18)
O4^{v}—K3—C23^{iv}	125.21(19)	O5—K1—Zr1	31.92(10)
O1—K3—C23^{iv}	126.39(17)	O9—K1—Zr1	32.77(10)
O16^{iv}—K3—C23^{iv}	43.77(16)	O3^{iv}—K1—Zr1	120.04(16)
O10—K3—C23^{iv}	80.03(16)	O4^{iv}—K1—Zr1	118.72(14)
O6—K3—C23^{iv}	78.62(15)	O16^{ix}—K1—Zr1	103.11(12)
C1—K3—C23^{iv}	147.18(19)	O14—K1—Zr1	34.65(9)
O15^{iv}—K3—C22^{iv}	42.63(16)	C15^{x}—K1—Zr1	146.79(15)
O4^{v}—K3—C22^{iv}	99.72(19)	C5^{iv}—K1—Zr1	110.00(14)
O1—K3—C22^{iv}	137.63(17)	C13—K1—Zr1	48.57(11)
O16^{iv}—K3—C22^{iv}	19.41(15)	C4^{iv}—K1—Zr1	108.67(14)
O10—K3—C22^{iv}	77.56(15)	O5—K1—K4^{i}	89.59(11)
O6—K3—C22^{iv}	96.91(15)	O9—K1—K4^{i}	39.56(10)
C1—K3—C22^{iv}	148.65(18)	O3^{iv}—K1—K4^{i}	156.43(16)
C23^{iv}—K3—C22^{iv}	25.50(17)	O4^{iv}—K1—K4^{i}	103.83(14)
O15^{iv}—K3—Zr1	101.68(13)	O16^{ix}—K1—K4^{i}	46.36(11)
O4^{v}—K3—Zr1	99.40(15)	O14—K1—K4^{i}	43.68(9)
O1—K3—Zr1	31.75(10)	C15^{x}—K1—K4^{i}	102.57(15)
O16^{iv}—K3—Zr1	117.24(12)	C5^{iv}—K1—K4^{i}	137.41(16)
O10—K3—Zr1	32.46(9)	C13—K1—K4^{i}	51.35(12)
O6—K3—Zr1	33.17(8)	C4^{iv}—K1—K4^{i}	114.15(15)
C1—K3—Zr1	48.52(12)	Zr1—K1—K4^{i}	57.68(4)
C23^{iv}—K3—Zr1	98.85(13)	O8—K4—O9^{ii}	100.3(2)
C22^{iv}—K3—Zr1	105.91(13)	O8—K4—O12^{xi}	102.1(2)
O15^{iv}—K3—K1^{vi}	101.07(12)	O9^{ii}—K4—O12^{xi}	151.67(17)
O4^{v}—K3—K1^{vi}	42.40(14)	O8—K4—O2^{ii}	98.84(19)
O1—K3—K1^{vi}	115.31(11)	O9^{ii}—K4—O2^{ii}	59.08(14)
O16^{iv}—K3—K1^{vi}	43.76(11)	O12^{xi}—K4—O2^{ii}	100.32(18)
O10—K3—K1^{vi}	72.13(11)	O8—K4—O14^{ii}	149.3(2)
O6—K3—K1^{vi}	123.34(10)	O9^{ii}—K4—O14^{ii}	51.85(13)
C1—K3—K1^{vi}	103.51(13)	O12^{xi}—K4—O14^{ii}	101.64(17)
C23^{iv}—K3—K1^{vi}	83.61(13)	O2^{ii}—K4—O14^{ii}	57.83(15)
C22^{iv}—K3—K1^{vi}	58.48(12)	O8—K4—O16^{xii}	97.30(17)
Zr1—K3—K1^{vi}	100.31(5)	O9^{ii}—K4—O16^{xii}	76.07(14)
O15^{iv}—K3—K2	92.12(12)	O12^{xi}—K4—O16^{xii}	117.53(18)
O4^{v}—K3—K2	126.84(15)	O2^{ii}—K4—O16^{xii}	134.28(15)
O1—K3—K2	39.06(10)	O14^{ii}—K4—O16^{xii}	88.59(15)
O16^{iv}—K3—K2	148.80(12)	O8—K4—O7	52.69(19)
O10—K3—K2	84.09(11)	O9^{ii}—K4—O7	123.02(15)
O6—K3—K2	38.47(9)	O12^{xi}—K4—O7	84.63(17)
C1—K3—K2	55.51(12)	O2^{ii}—K4—O7	151.32(17)
C23^{iv}—K3—K2	105.32(13)	O14^{ii}—K4—O7	149.25(15)
C22^{iv}—K3—K2	129.45(13)	O16^{xii}—K4—O7	62.42(15)
Zr1—K3—K2	53.47(3)	O8—K4—C22^{xii}	101.78(19)
K1^{vi}—K3—K2	152.89(6)	O9^{ii}—K4—C22^{xii}	96.49(16)
C7—C12—C11	120.2(8)	O12^{xi}—K4—C22^{xii}	95.6(2)
C7—C12—H12	119.900	O2^{ii}—K4—C22^{xii}	150.60(17)
C11—C12—H12	119.900	O14^{ii}—K4—C22^{xii}	94.89(16)
O16—C22—C21	123.1(6)	O16^{xii}—K4—C22^{xii}	21.99(15)
O16—C22—C23	118.7(6)	O7—K4—C22^{xii}	54.40(16)
C21—C22—C23	118.1(6)	O8—K4—C21^{xii}	121.1(2)
O16—C22—K4^{vii}	65.9(4)	O9^{ii}—K4—C21^{xii}	105.22(17)
C21—C22—K4^{vii}	78.3(4)	O12^{xi}—K4—C21^{xii}	77.37(19)
C23—C22—K4^{vii}	133.4(5)	O2^{ii}—K4—C21^{xii}	139.78(17)
O16—C22—K3^{iii}	49.2(4)	O14^{ii}—K4—C21^{xii}	82.99(16)

C21—C22—K3^{iii}	153.4(5)	O16^{xii}—K4—C21^{xii}	42.56(15)
C23—C22—K3^{iii}	74.2(4)	O7—K4—C21^{xii}	68.90(16)
K4^{vii}—C22—K3^{iii}	111.4(2)	C22^{xii}—K4—C21^{xii}	24.30(17)
C19—C24—C23	119.2(6)	O8—K4—C13^{ii}	79.5(2)
C19—C24—H24	120.400	O9^{ii}—K4—C13^{ii}	21.14(14)
C23—C24—H24	120.400	O12^{xi}—K4—C13^{ii}	166.38(19)
O14—C20—C21	124.5(6)	O2^{ii}—K4—C13^{ii}	66.14(15)
O14—C20—C19	113.6(6)	O14^{ii}—K4—C13^{ii}	72.94(15)
C21—C20—C19	121.7(6)	O16^{xii}—K4—C13^{ii}	75.31(15)
O9—C13—C18	123.8(7)	O7—K4—C13^{ii}	106.50(16)
O9—C13—C14	113.6(6)	C22^{xii}—K4—C13^{ii}	97.31(17)
C18—C13—C14	122.6(6)	C21^{xii}—K4—C13^{ii}	113.62(17)
O9—C13—K4^{i}	49.1(3)	O8—K4—C10	17.70(19)
C18—C13—K4^{i}	92.3(5)	O9^{ii}—K4—C10	96.39(18)
C14—C13—K4^{i}	130.0(4)	O12^{xi}—K4—C10	110.1(2)
O9—C13—K1	46.4(3)	O2^{ii}—K4—C10	111.8(2)
C18—C13—K1	91.0(4)	O14^{ii}—K4—C10	148.12(18)
C14—C13—K1	131.2(4)	O16^{xii}—K4—C10	79.60(18)
K4^{i}—C13—K1	75.50(15)	O7—K4—C10	41.63(19)
C11—O7—K2^{iv}	112.9(5)	C22^{xii}—K4—C10	85.15(19)
C11—O7—K4	106.3(5)	C21^{xii}—K4—C10	106.4(2)
K2^{iv}—O7—K4	79.25(16)	C13^{ii}—K4—C10	75.44(19)
C8—C9—C10	119.9(8)	O8—K4—K2^{iv}	53.49(18)
C8—C9—H9	120.100	O9^{ii}—K4—K2^{iv}	153.79(12)
C10—C9—H9	120.100	O12^{xi}—K4—K2^{iv}	51.09(14)
C2—C3—C4	120.2(8)	O2^{ii}—K4—K2^{iv}	118.59(12)
C2—C3—H3	119.900	O14^{ii}—K4—K2^{iv}	152.64(11)
C4—C3—H3	119.900	O16^{xii}—K4—K2^{iv}	105.38(11)
O2—C2—C3	127.3(7)	O7—K4—K2^{iv}	44.83(10)
O2—C2—C1	112.0(6)	C22^{xii}—K4—K2^{iv}	90.62(13)
C3—C2—C1	120.7(7)	C21^{xii}—K4—K2^{iv}	91.52(13)
C16—O12—K4^{viii}	122.1(6)	C13^{ii}—K4—K2^{iv}	132.89(13)
C16—O12—K2^{i}	114.9(6)	C10—K4—K2^{iv}	59.01(15)
K4^{viii}—O12—K2^{i}	82.49(18)	O3—C5—C6	123.2(9)
C14—C15—C16	121.1(8)	O3—C5—C4	118.0(7)
C14—C15—K1^{vi}	119.6(5)	C6—C5—C4	118.7(8)
C16—C15—K1^{vi}	96.8(5)	O3—C5—K1^{iii}	47.6(5)
C14—C15—H15	119.400	C6—C5—K1^{iii}	144.5(6)
C16—C15—H15	119.400	C4—C5—K1^{iii}	80.1(4)
K1^{vi}—C15—H15	51.400	O12—C16—C15	122.4(9)
O6—C8—C9	124.5(7)	O12—C16—C17	117.9(8)
O6—C8—C7	113.9(6)	C15—C16—C17	119.7(7)

(i) 1.5-x, -0.5+y, z; (ii) 1.5-x, 0.5+y, z; (iii) 0.5+x, y, 0.5-z; (iv) -0.5+x, y, 0.5-z;
(v) 2-x, -y, 1-z; (vi) 1.5-x, -y, 0.5+z; (vii) 0.5+x, 0.5-y, -z; (viii) 1-x, -0.5+y, 0.5-z;
(ix) 2-x, -y, -z; (x) 1.5-x, -y, -0.5+z; (xi) 1-x, 0.5+y, 0.5-z; (xii) -0.5+x, 0.5-y, -z;
(xiii) x, 0.5-y, 0.5+z; (xiv) x, 0.5-y, -0.5+z.

- Kx···Oy and Kx···Oz distances and Oy−Kx−Oz angles for compound **1b**.

Kx	**Oy**	**Dist (Kx···Oy) (Å)**	**Oz**	**Dist (Kx···Oz) (Å)**	**Angle (Oy···Kx···Oz) (°)**
K2	O11^{ii}	2.63(7)	O7^{iii}	2.70(6)	134.2(2)
	O11^{ii}	2.63(7)	O13	2.71(5)	93.9(2)
	O11^{ii}	2.63(7)	O6	2.79(5)	81.2(2)
	O11^{ii}	2.63(7)	O1	2.90(5)	133.2(2)
	O7^{iii}	2.70(6)	O13	2.71(5)	112.4(2)
	O7^{iii}	2.70(6)	O6	2.79(5)	144.0(2)

	$O7^{iii}$	2.70(6)	O1	2.90(5)	92.6(2)
	$O7^{iii}$	2.70(6)	$O12^{ii}$	2.96(6)	89.9(2)
	O13	2.71(5)	$O12^{ii}$	2.96(6)	151.1(2)
	O6	2.79(5)	$O12^{ii}$	2.96(6)	110.6(2)
	O1	2.90(5)	$O12^{ii}$	2.96(6)	141.8(2)
K3	$O15^{iv}$	2.65(5)	$O4^{v}$	2.65(6)	140.8(2)
	$O15^{iv}$	2.65(5)	O1	2.79(5)	122.1(2)
	$O15^{iv}$	2.65(5)	O10	2.86(5)	91.4(2)
	$O4^{v}$	2.65(6)	O1	2.79(5)	92.3(2)
	$O4^{v}$	2.65(6)	$O16^{iv}$	2.85(6)	82.2(2)
	$O4^{v}$	2.65(6)	O10	2.86(5)	89.0(2)
	O1	2.79(5)	$O16^{iv}$	2.85(6)	147.3(2)
	O16	2.85(6)	O10	2.86(5)	85.5(2)
K1	O5	2.75(5)	$O3^{iv}$	2.76(7)	90.8(2)
	O5	2.75(5)	$O4^{iv}$	2.99(6)	114.1(2)
	O9	2.76(5)	$O3^{iv}$	2.76(7)	124.0(2)
	O9	2.76(5)	$O4^{iv}$	2.99(6)	93.3(2)
K4	O8	2.66(8)	$O9^{i}$	2.73(5)	100.3(2)
	O8	2.66(8)	$O12^{ii}$	2.75(7)	102.2(2)
	O8	2.66(8)	$O2^{ii}$	2.79(5)	98.9(2)
	O8	2.66(8)	$O14^{ii}$	2.91(4)	149.3(2)
	$O9^{ii}$	2.73(5)	$O12^{xi}$	2.75(7)	151.6(2)
	$O12^{iv}$	2.75(7)	$O2^{ii}$	2.79(5)	100.3(2)
	$O12^{iv}$	2.75(7)	$O14^{ii}$	2.91(4)	101.6(2)

Figure S3. Graphical representation of the O−K−O angle distribution in **1a** (top) and **1b** (bottom).

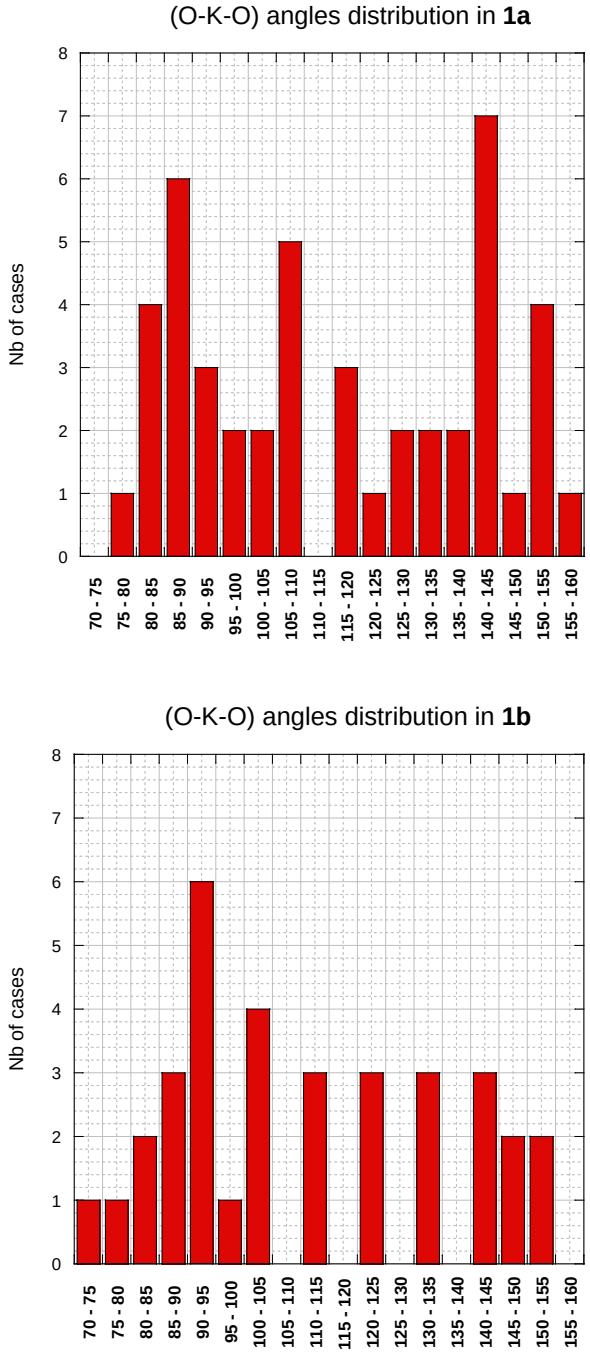
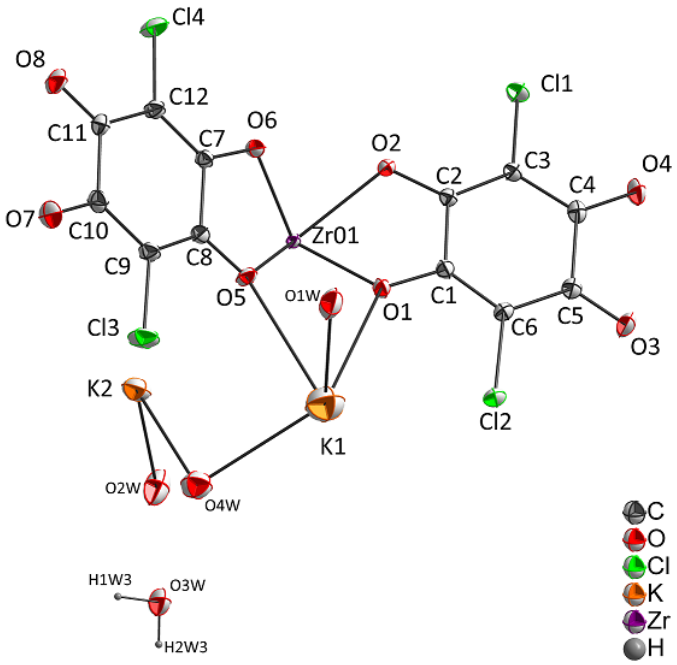


Figure S4. Ortep view of the asymmetric unit of $\{K_4[Zr(CA)_4]\}$ $7H_2O$ (**2**) with ellipsoids cut at the 30% probability level.



Tables S3. Selected bond lengths (Å) and angles (°) for compound **2**:

- Selected metric data for compound **2**.

Atoms 1,2	d 1,2 (Å)	Atoms 1,2	d 1,2 (Å)
C1—O1	1.295(5)	O5—Zr01	2.224(3)
C1—C6	1.362(6)	O5—K1	2.953(3)
C1—C2	1.499(6)	O5—K2	3.260(3)
C2—O2	1.292(5)	O4W—K2	2.824(5)
C2—C3	1.369(6)	O4W—K1	2.880(5)
C3—C4	1.425(6)	O6—Zr01	2.186(3)
C3—Cl1	1.725(4)	O6—K2^{i}	2.787(3)
C4—O4	1.223(6)	O7—K2^{v}	2.877(4)
C4—C5	1.562(6)	O7—K2^{vi}	3.385(4)
C5—O3	1.227(6)	Cl1—K1^{i}	3.547(3)
C5—C6	1.416(6)	Cl2—K1	3.477(3)
C6—Cl2	1.730(4)	Cl3—K2	3.522(2)
C7—O6	1.283(5)	Cl4—K2^{i}	3.3780(18)
C7—C12	1.363(6)	K1—O4^{vii}	2.923(4)
C7—C8	1.507(6)	K1—O2^{i}	3.392(4)
C8—O5	1.293(5)	K1—O4^{iv}	3.396(5)
C8—C9	1.359(6)	K1—Cl1^{i}	3.547(3)
C9—C10	1.440(6)	K1—Zr01	4.223(2)
C9—Cl3	1.718(4)	K1—K2	4.224(3)
C10—O7	1.218(5)	K1—K1^{viii}	4.249(4)
C10—C11	1.558(6)	K2—O6^{i}	2.787(3)
C11—O8	1.224(6)	K2—O7^{v}	2.877(4)
C11—C12	1.429(6)	K2—O2^{i}	2.982(3)
C12—Cl4	1.719(4)	K2—Cl4^{i}	3.3780(18)
O1—Zr01	2.169(3)	K2—O7^{ix}	3.385(4)
O1—K1	2.990(4)	K2—Zr01	4.0853(13)
O2—Zr01	2.226(3)	K2—K2^{ii}	4.290(3)

O2—K2^{i}	2.982(3)	Zr01—O1^{i}	2.169(3)
O2—K1^{i}	3.392(4)	Zr01—O6^{i}	2.186(3)
O1W—K1	2.930(5)	Zr01—O5^{i}	2.224(3)
O2W—K2^{ii}	2.652(4)	Zr01—O2^{i}	2.226(3)
O2W—K2	2.652(4)	Zr01—K2^{i}	4.0853(13)
O4—K1^{iii}	2.923(4)	Zr01—K1^{i}	4.223(2)
O4—K1^{iv}	3.396(5)		

Atoms 1,2,3	Angle 1,2,3 (°)	Atoms 1,2,3	Angle 1,2,3 (°)
O1—C1—C6	124.0(4)	O2W—K2—O6^{i}	109.91(8)
O1—C1—C2	113.7(4)	O2W—K2—O4W	88.33(12)
C6—C1—C2	122.1(4)	O6^{i}—K2—O4W	132.60(12)
O2—C2—C3	127.1(4)	O2W—K2—O7^{v}	71.77(10)
O2—C2—C1	113.9(3)	O6^{i}—K2—O7^{v}	150.74(12)
C3—C2—C1	118.9(4)	O4W—K2—O7^{v}	75.94(13)
C2—C3—C4	122.0(4)	O2W—K2—O2^{i}	77.92(11)
C2—C3—Cl1	120.4(3)	O6^{i}—K2—O2^{i}	56.79(8)
C4—C3—Cl1	117.5(3)	O4W—K2—O2^{i}	87.23(11)
O4—C4—C3	125.1(4)	O7^{v}—K2—O2^{i}	145.48(10)
O4—C4—C5	116.7(4)	O2W—K2—O5	131.12(12)
C3—C4—C5	118.1(4)	O6^{i}—K2—O5	51.51(8)
O3—C5—C6	124.4(4)	O4W—K2—O5	83.17(11)
O3—C5—C4	118.3(4)	O7^{v}—K2—O5	148.78(11)
C6—C5—C4	117.3(4)	O2^{i}—K2—O5	53.72(8)
C1—C6—C5	121.3(4)	O2W—K2—Cl4^{i}	126.92(10)
C1—C6—Cl2	119.8(3)	O6^{i}—K2—Cl4^{i}	56.98(7)
C5—C6—Cl2	118.9(3)	O4W—K2—Cl4^{i}	140.92(10)
O6—C7—C12	124.8(4)	O7^{v}—K2—Cl4^{i}	97.74(9)
O6—C7—C8	114.0(3)	O2^{i}—K2—Cl4^{i}	113.76(7)
C12—C7—C8	121.0(4)	O5—K2—Cl4^{i}	84.01(6)
O5—C8—C9	126.5(4)	O2W—K2—O7^{ix}	63.7(1)
O5—C8—C7	113.7(3)	O6^{i}—K2—O7^{ix}	71.73(9)
C9—C8—C7	119.7(4)	O4W—K2—O7^{ix}	149.80(12)
C8—C9—C10	122.2(4)	O7^{v}—K2—O7^{ix}	84.15(12)
C8—C9—Cl3	119.7(3)	O2^{i}—K2—O7^{ix}	97.08(9)
C10—C9—Cl3	118.0(3)	O5—K2—O7^{ix}	123.24(9)
O7—C10—C9	125.1(4)	Cl4^{i}—K2—O7^{ix}	63.51(7)
O7—C10—C11	117.3(4)	O2W—K2—Cl3	149.70(8)
C9—C10—C11	117.5(4)	O6^{i}—K2—Cl3	93.90(8)
O8—C11—C12	124.4(4)	O4W—K2—Cl3	61.47(10)
O8—C11—C10	118.0(4)	O7^{v}—K2—Cl3	96.65(9)
C12—C11—C10	117.6(4)	O2^{i}—K2—Cl3	101.44(7)
C7—C12—C11	121.7(4)	O5—K2—Cl3	52.57(6)
C7—C12—Cl4	119.9(3)	Cl4^{i}—K2—Cl3	81.55(4)
C11—C12—Cl4	118.3(3)	O7^{ix}—K2—Cl3	144.75(8)
C1—O1—Zr01	116.6(3)	O2W—K2—Zr01	105.81(8)
C1—O1—K1	133.5(3)	O6^{i}—K2—Zr01	30.21(6)
Zr01—O1—K1	108.86(12)	O4W—K2—Zr01	103.65(10)
C2—O2—Zr01	115.3(2)	O7^{v}—K2—Zr01	177.52(9)
C2—O2—K2^{i}	140.7(3)	O2^{i}—K2—Zr01	32.16(6)
Zr01—O2—K2^{i}	102.35(10)	O5—K2—Zr01	32.87(5)
C2—O2—K1^{i}	103.5(2)	Cl4^{i}—K2—Zr01	84.13(3)
Zr01—O2—K1^{i}	95.21(10)	O7^{ix}—K2—Zr01	95.26(7)
K2^{i}—O2—K1^{i}	82.73(8)	Cl3—K2—Zr01	85.22(4)
K2^{ii}—O2W—K2	108.0(2)	O2W—K2—K1	102.77(11)
C4—O4—K1^{iii}	157.9(4)	O6^{i}—K2—K1	89.96(7)
C4—O4—K1^{iv}	117.8(3)	O4W—K2—K1	42.75(10)
K1^{iii}—O4—K1^{iv}	84.16(11)	O7^{v}—K2—K1	118.64(10)
C8—O5—Zr01	116.0(2)	O2^{i}—K2—K1	52.81(7)
C8—O5—K1	134.6(3)	O5—K2—K1	44.18(6)
Zr01—O5—K1	108.53(11)	Cl4^{i}—K2—K1	126.08(5)
C8—O5—K2	98.9(2)	O7^{ix}—K2—K1	149.82(8)
Zr01—O5—K2	94.43(10)	Cl3—K2—K1	57.43(5)

K1—O5—K2	85.52(9)	Zr01—K2—K1	61.07(3)
K2—O4W—K1	95.54(14)	O2W—K2—K2^{ii}	36.02(11)
C7—O6—Zr01	116.8(2)	O6^{i}—K2—K2^{ii}	111.62(8)
C7—O6—K2^{i}	132.6(3)	O4W—K2—K2^{ii}	108.33(10)
Zr01—O6—K2^{i}	109.88(11)	O7^{v}—K2—K2^{ii}	51.92(9)
C10—O7—K2^{v}	136.1(3)	O2^{i}—K2—K2^{ii}	108.37(7)
C10—O7—K2^{vi}	130.9(3)	O5—K2—K2^{ii}	159.21(7)
K2^{v}—O7—K2^{vi}	86.09(10)	Cl4^{i}—K2—K2^{ii}	96.22(4)
C3—Cl1—K1^{i}	93.29(16)	O7^{ix}—K2—K2^{ii}	41.99(7)
C6—Cl2—K1	105.18(16)	Cl3—K2—K2^{ii}	148.13(5)
C9—Cl3—K2	86.95(16)	Zr01—K2—K2^{ii}	126.37(5)
C12—Cl4—K2^{i}	101.52(15)	K1—K2—K2^{ii}	137.26(4)
O4W—K1—O4^{vii}	79.16(13)	O1—Zr01—O1^{i}	86.53(17)
O4W—K1—O1W	119.14(14)	O1—Zr01—O6	108.30(12)
O4^{vii}—K1—O1W	107.65(14)	O1^{i}—Zr01—O6	141.14(11)
O4W—K1—O5	87.97(12)	O1—Zr01—O6^{i}	141.14(11)
O4^{vii}—K1—O5	166.44(13)	O1^{i}—Zr01—O6^{i}	108.30(12)
O1W—K1—O5	74.87(11)	O6—Zr01—O6^{i}	82.77(16)
O4W—K1—O1	126.31(13)	O1—Zr01—O5^{i}	147.82(11)
O4^{vii}—K1—O1	139.00(13)	O1^{i}—Zr01—O5^{i}	74.83(11)
O1W—K1—O1	88.14(12)	O6—Zr01—O5^{i}	74.25(11)
O5—K1—O1	53.38(9)	O6^{i}—Zr01—O5^{i}	70.67(10)
O4W—K1—O2^{i}	78.93(12)	O1—Zr01—O5	74.83(11)
O4^{vii}—K1—O2^{i}	127.72(12)	O1^{i}—Zr01—O5	147.82(11)
O1W—K1—O2^{i}	124.50(12)	O6—Zr01—O5	70.67(10)
O5—K1—O2^{i}	52.44(8)	O6^{i}—Zr01—O5	74.25(11)
O1—K1—O2^{i}	48.75(8)	O5^{i}—Zr01—O5	132.66(15)
O4W—K1—O4^{iv}	134.86(13)	O1—Zr01—O2^{i}	74.44(12)
O4^{vii}—K1—O4^{iv}	63.25(14)	O1^{i}—Zr01—O2^{i}	70.73(11)
O1W—K1—O4^{iv}	57.05(11)	O6—Zr01—O2^{i}	147.18(10)
O5—K1—O4^{iv}	125.96(11)	O6^{i}—Zr01—O2^{i}	77.06(11)
O1—K1—O4^{iv}	98.79(10)	O5^{i}—Zr01—O2^{i}	121.36(11)
O2^{i}—K1—O4^{iv}	143.95(11)	O5—Zr01—O2^{i}	79.01(11)
O4W—K1—Cl2	136.14(12)	O1—Zr01—O2	70.73(10)
O4^{vii}—K1—Cl2	84.98(9)	O1^{i}—Zr01—O2	74.44(12)
O1W—K1—Cl2	104.59(10)	O6—Zr01—O2	77.06(11)
O5—K1—Cl2	107.52(9)	O6^{i}—Zr01—O2	147.18(10)
O1—K1—Cl2	54.17(7)	O5^{i}—Zr01—O2	79.01(11)
O2^{i}—K1—Cl2	79.19(7)	O5—Zr01—O2	121.36(11)
O4^{iv}—K1—Cl2	67.07(8)	O2^{i}—Zr01—O2	131.49(15)
O4W—K1—Cl1^{i}	61.79(10)	O1—Zr01—K2^{i}	108.05(8)
O4^{vii}—K1—Cl1^{i}	75.61(10)	O1^{i}—Zr01—K2^{i}	101.71(8)
O1W—K1—Cl1^{i}	176.66(11)	O6—Zr01—K2^{i}	39.90(8)
O5—K1—Cl1^{i}	102.14(9)	O6^{i}—Zr01—K2^{i}	103.81(8)
O1—K1—Cl1^{i}	88.85(9)	O5^{i}—Zr01—K2^{i}	52.70(8)
O2^{i}—K1—Cl1^{i}	52.20(6)	O5—Zr01—K2^{i}	108.86(8)
O4^{iv}—K1—Cl1^{i}	124.95(10)	O2^{i}—Zr01—K2^{i}	172.08(8)
Cl2—K1—Cl1^{i}	74.75(6)	O2—Zr01—K2^{i}	45.48(7)
O4W—K1—Zr01	99.41(11)	O1—Zr01—K2	101.71(8)
O4^{vii}—K1—Zr01	156.85(11)	O1^{i}—Zr01—K2	108.05(8)
O1W—K1—Zr01	93.33(10)	O6—Zr01—K2	103.81(8)
O5—K1—Zr01	29.95(6)	O6^{i}—Zr01—K2	39.90(8)
O1—K1—Zr01	29.08(6)	O5^{i}—Zr01—K2	108.86(8)
O2^{i}—K1—Zr01	31.67(5)	O5—Zr01—K2	52.70(8)
O4^{iv}—K1—Zr01	125.03(9)	O2^{i}—Zr01—K2	45.48(7)
Cl2—K1—Zr01	80.23(5)	O2—Zr01—K2	172.08(8)
Cl1^{i}—K1—Zr01	83.33(5)	K2^{i}—Zr01—K2	138.76(4)
O4W—K1—K2	41.72(10)	O1—Zr01—K1	42.06(8)
O4^{vii}—K1—K2	118.61(11)	O1^{i}—Zr01—K1	108.35(8)
O1W—K1—K2	114.07(10)	O6—Zr01—K1	106.22(8)
O5—K1—K2	50.30(7)	O6^{i}—Zr01—K1	99.28(8)
O1—K1—K2	85.94(8)	O5^{i}—Zr01—K1	169.89(8)
O2^{i}—K1—K2	44.45(6)	O5—Zr01—K1	41.52(8)

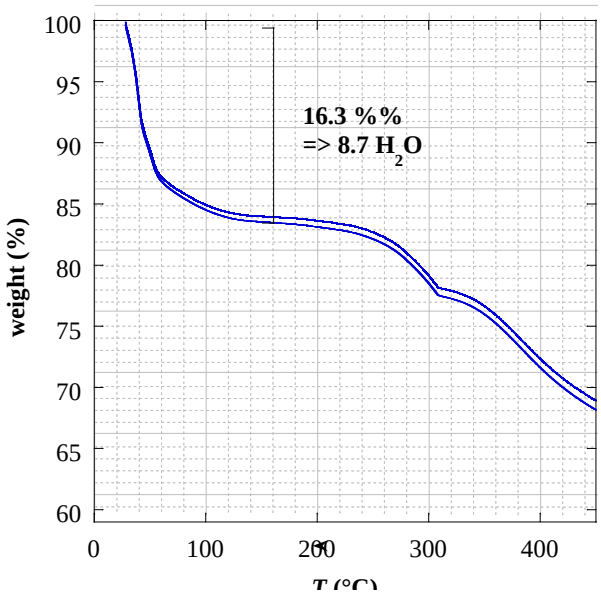
O4^{iv}—K1—K2	169.47(10)	O2^{i}—Zr01—K1	53.12(8)
Cl2—K1—K2	122.82(7)	O2—Zr01—K1	111.03(8)
Cl1^{i}—K1—K2	64.23(5)	K2^{i}—Zr01—K1	133.66(4)
Zr01—K1—K2	57.85(3)	K2—Zr01—K1	61.08(4)
O4W—K1—K1^{viii}	94.48(11)	O1—Zr01—K1^{i}	108.35(8)
O4^{vii}—K1—K1^{viii}	52.66(9)	O1^{i}—Zr01—K1^{i}	42.06(8)
O1W—K1—K1^{viii}	56.36(10)	O6—Zr01—K1^{i}	99.28(8)
O5—K1—K1^{viii}	125.12(8)	O6^{i}—Zr01—K1^{i}	106.22(8)
O1—K1—K1^{viii}	136.86(11)	O5^{i}—Zr01—K1^{i}	41.52(8)
O2^{i}—K1—K1^{viii}	172.84(9)	O5—Zr01—K1^{i}	169.89(8)
O4^{iv}—K1—K1^{viii}	43.18(7)	O2^{i}—Zr01—K1^{i}	111.03(8)
Cl2—K1—K1^{viii}	107.73(5)	O2—Zr01—K1^{i}	53.12(8)
Cl1^{i}—K1—K1^{viii}	126.98(8)	K2^{i}—Zr01—K1^{i}	61.08(4)
Zr01—K1—K1^{viii}	149.59(7)	K2—Zr01—K1^{i}	133.66(4)
K2—K1—K1^{viii}	128.40(6)	K1—Zr01—K1^{i}	145.85(7)

(i) 2-x, y, 0.5-z; (ii) 3-x, y, 0.5-z; (iii) -1+x, 1-y, -0.5+z; (iv) 2-x, 1-y, 1-z; (v) 3-x, -y, 1-z; (vi) x, -y, 0.5+z; (vii) 1+x, 1-y, 0.5+z; (viii) 3-x, y, 1.5-z; (ix) x, -y, -0.5+z.

- Kx···Oy and Kx···Oz distances and Oy−Kx−Oz angles for compound **2**.

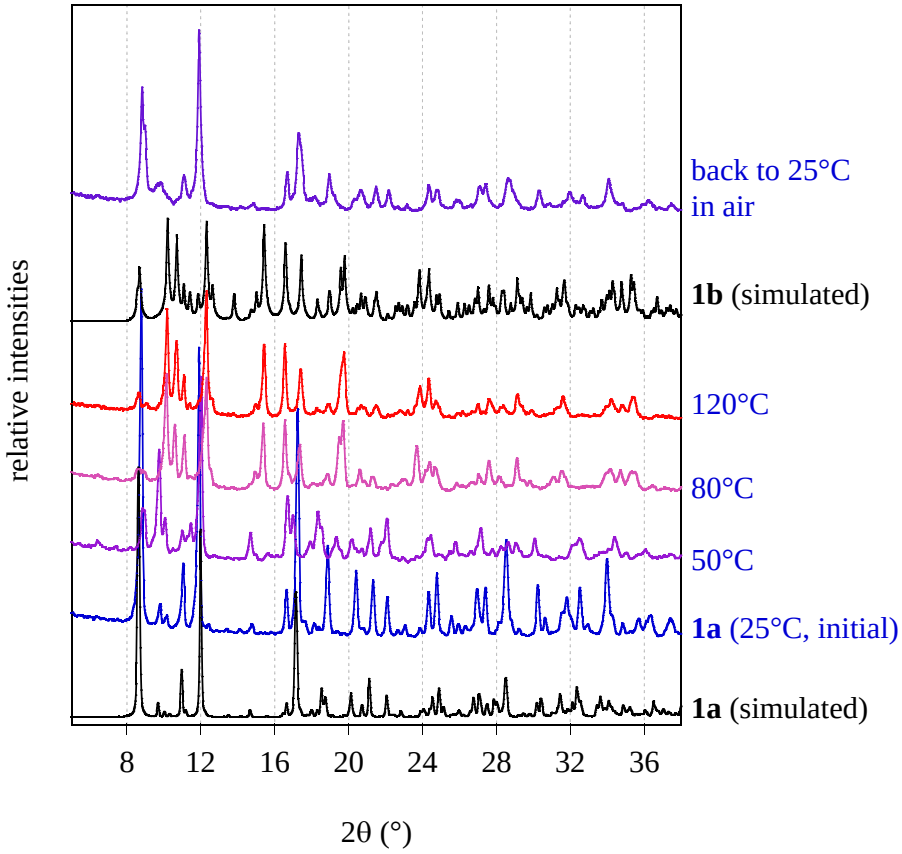
Kx	**Oy**	**Dist (Kx···Oy) (Å)**	**Oz**	**Dist (Kx···Oz) (Å)**	**Angle (Oy···Kx···Oz) (°)**
K1	O4^{vii}	2.92(4)	O5	2.95(3)	166.5(1)
	O4^{vii}	2.92(4)	O11	2.99(3)	139.0(2)
K2	O6^{i}	2.79(3)	O7^{v}	2.88(5)	150.7(1)
	O7^{v}	2.88(5)	O2^{i}	2.98(3)	145.5(1)

Figure S5. Thermogravimetric analysis for **1a**.



TGA was carried out under N_2 stream, a heating of 1°C/min was applied from 26 to 300°C and 10°C/min between 300 and 600°C.

Figure S6. Temperature dependence of the X-ray diffractogram for **1a** in air.



Powder X-ray diffraction patterns were recorded on a *Philips X-Pert* (θ-2θ mode) diffractometer coupled to an Anton Parr oven with heating of 1°C/min rate. All data were collected in $5° < 2\theta < 50°$ range, with 0.02 steps and 10 s of exposure.

Figure S7. N_2 adsorption isotherm obtained at 77 K for **1b**.

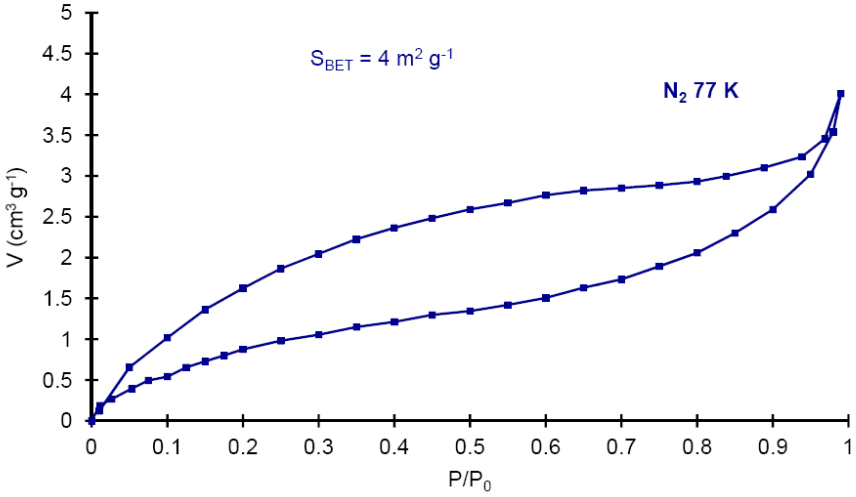


Figure S8. Isosteric heat of adsorption of CO_2 for **1b**.