Supporting Information

Synthesis, structure, and magnetic properties of new layered phosphate halides $Sr_2Cu_5(PO_4)_4X_2 \cdot 8H_2O$ (X =Cl, Br) with a crown-like building unit

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Figure S1. Experimental (Black line) and Simulated (Red line) powder X-ray diffraction patterns of $Sr_2Cu_5(PO_4)_4X_2 \cdot 8H_2O$ [X = (a) Cl and (b) Br].

Figure S2. The χ^{-1} versus T curves of $Sr_2Cu_5(PO_4)_4X_2 \cdot 8H_2O$ [X = (a) Cl and (b) Br].

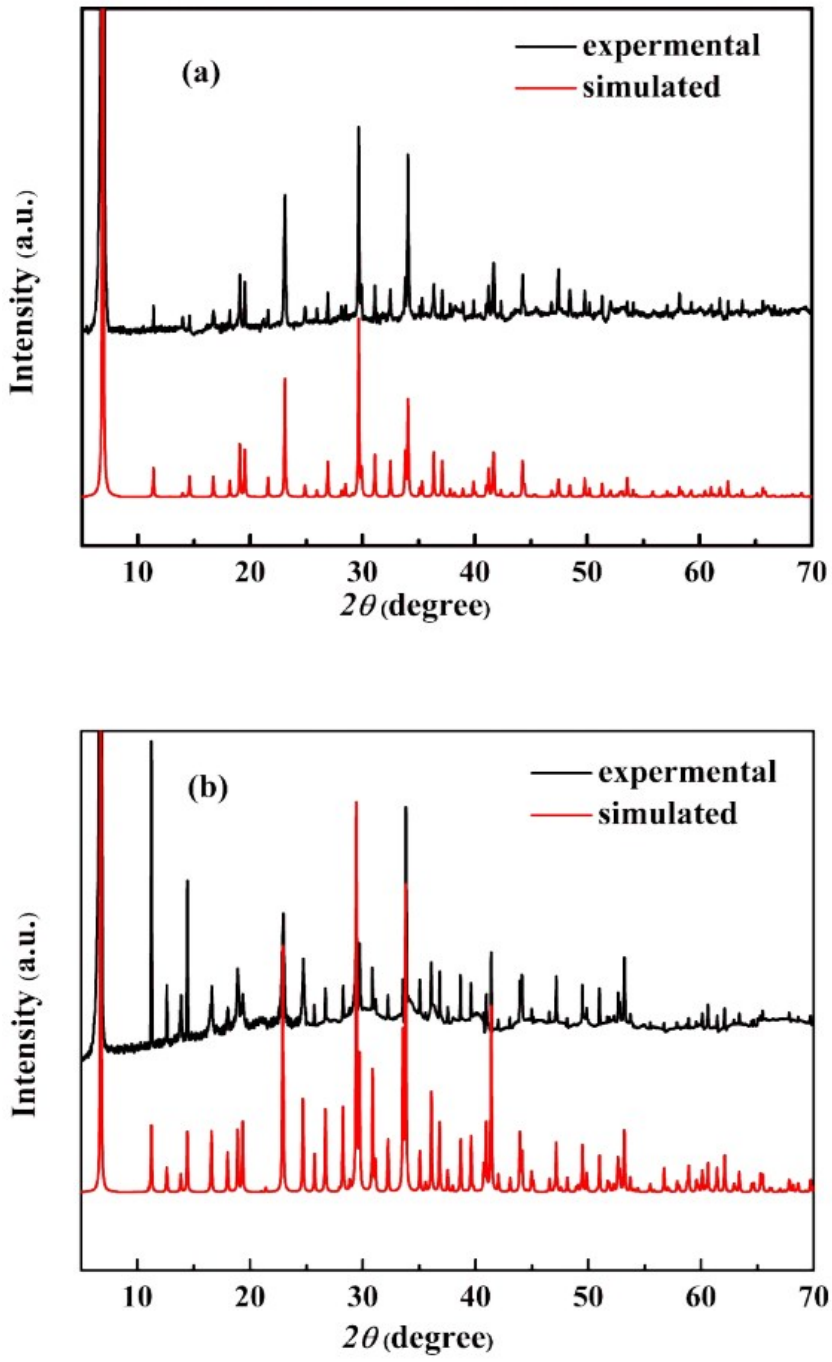
Figure S3. The fit of square-lattice Heisenberg antiferromagnetic spin model for magnetic susceptibility data of $Sr_2Cu_5(PO_4)_4X_2 \cdot 8H_2O$ [X = (a) Cl and (b) Br].

Table S1. The Wyckoff positions, atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $Sr_2Cu_5(PO_4)_4X_2 \cdot 8H_2O$ (X = Cl and Br). U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Table S2. Anisotropic displacement parameters ($Å^2 \times 10^3$) for $Sr_2Cu_5(PO_4)_4X_2 \cdot 8H_2O$ (X = Cl and Br). The anisotropic displacement factor exponent takes the form: $-2\pi^2$ [$h^2 a^{*2} U11 + ... + 2 h k a^* b^* U12$].

Table S3. Bond lengths [Å] and angles [deg] for $Sr_2Cu_5(PO_4)_4Cl_2 \cdot 8H_2O$.

Table S4. Bond lengths [Å] and angles [deg] for $Sr_2Cu_5(PO_4)_4Br_2 \cdot 8H_2O$.



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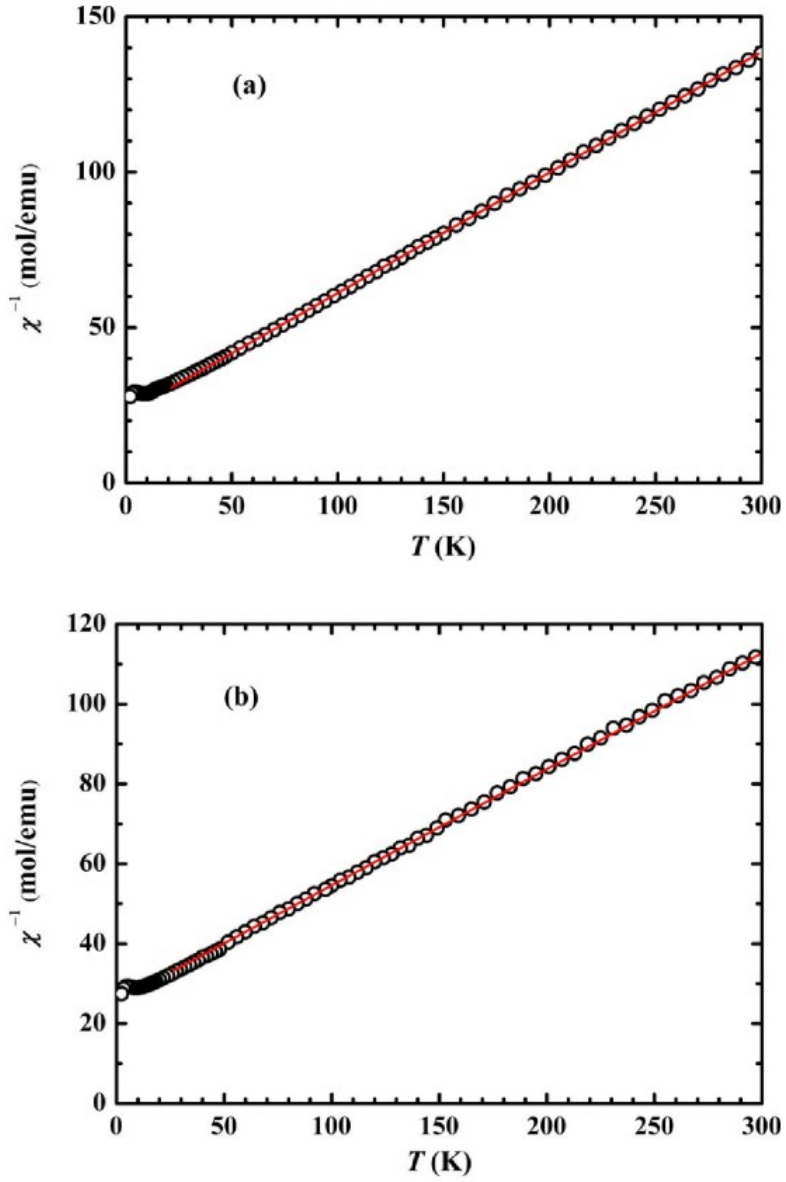

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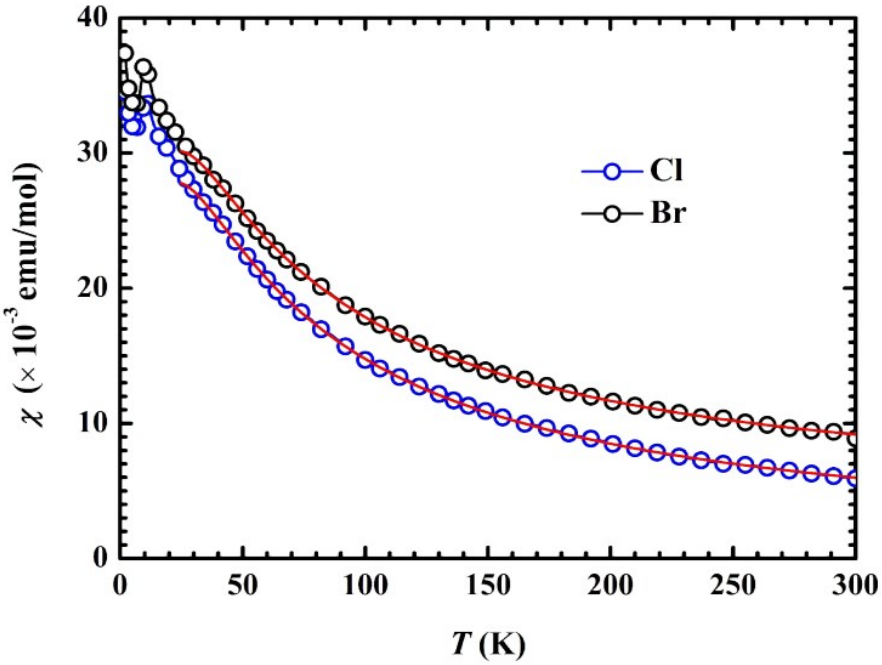

Figure S3. The fit of square-lattice Heisenberg antiferromagnetic spin model for magnetic susceptibility data of $Sr_2Cu_5(PO_4)_4X_2 \cdot 8H_2O$ [X = (a) Cl and (b) Br].

Table S1. The Wyckoff positions, atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (Å^2 ×10^3) for $Sr_2Cu_5(PO_4)_4X_2 \cdot 8H_2O$ (X =Cl, Br) . U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

atom	Wyck.	Site	x	y	z	U(eq)
Cu(1)	8g	1	7690(1)	4862(1)	10542(1)	13(1)
Cu(2)	2c	4..	10000	5000	7594(1)	12(1)
Cl(1)	2c	4..	10000	5000	11778(2)	19(1)
Cl(2)	8g	1	10000	5000	5334(2)	39(1)
P(1)	8g	1	7791(1)	6903(1)	8613(1)	11(1)
O(1)	8g	1	8475(3)	6342(3)	9656(2)	12(1)
O(2)	8g	1	6841(3)	3461(3)	11450(3)	14(1)
O(3)	8g	1	6628(3)	6228(3)	11326(3)	17(1)
O(4)	8g	1	8315(3)	6110(3)	7644(2)	17(1)
O(5)	8g	1	9112(6)	8176(5)	5994(3)	62(1)
O(6)	8g	1	5893(6)	7305(6)	6287(4)	93(2)
Sr(1)	4d	2..	10000	10000	7358(1)	24(1)
Cu(1)	8i	.m.	5195(1)	7500	552(1)	15(1)
Cu(2)	2c	4mm	2500	2500	2375(1)	9(1)
Br(1)	2c	4mm	7500	7500	1947(1)	15(1)
Br(2)	2c	4mm	2500	2500	4745(1)	26(1)
P(1)	8j	..m	4552(1)	4552(1)	1372(1)	23(1)
O(1)	8j	..m	3929(2)	3929(2)	328(2)	14(1)
O(2)	16k	1	4231(2)	6105(2)	1375(2)	26(1)
O(3)	16k	1	4168(3)	3622(3)	2343(3)	11(1)
Sr(1)	4f	2mm.	2500	7500	2612(1)	16(1)
O(4A)	16k	1	4604(5)	6474(5)	3786(4)	33(1)
O(4B)	16k	1	1463(5)	5723(4)	3932(4)	37(1)

Table S2. Anisotropic displacement parameters ($Å^2 \times 10^3$) for $Sr_2Cu_5(PO_4)_4X_2 \cdot 8H_2O$ (X =Cl, Br). The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U11 + ... + 2 h k a^* b^* U12]$.

atom	U11	U22	U33	U23	U13	U12
Cu(1)	12(1)	8(1)	19(1)	1(1)	3(1)	0(1)
Cu(2)	9(1)	9(1)	18(1)	0	0	0
Cl(1)	18(1)	18(1)	22(1)	0	0	0
Cl(2)	43(1)	43(1)	29(1)	0	0	0
P(1)	8(1)	9(1)	17(1)	-2(1)	-1(1)	1(1)
O(1)	10(1)	10(1)	16(1)	0(1)	-1(1)	0(1)
O(2)	17(2)	9(2)	18(2)	-1(1)	4(1)	2(1)
O(3)	15(2)	10(2)	25(2)	1(1)	6(2)	2(1)
O(4)	13(2)	17(2)	20(2)	-6(1)	-1(1)	4(1)
O(5)	119(4)	34(2)	34(3)	0(2)	-19(3)	7(3)
O(6)	100(5)	100(5)	79(4)	62(4)	-41(3)	-56(4)
Sr(1)	18(1)	38(1)	18(1)	0	0	4(1)
Cu(1)	11(1)	26(1)	9(1)	0	3(1)	0
Cu(2)	8(1)	8(1)	13(1)	0	0	0
Br(1)	15(1)	15(1)	13(1)	0	0	0
Br(2)	29(1)	29(1)	20(1)	0	0	0
P(1)	31(1)	31(1)	6(1)	1(1)	1(1)	-26(1)
O(1)	17(1)	17(1)	9(1)	0(1)	0(1)	-7(1)
O(2)	25(1)	33(1)	20(1)	-15(1)	13(1)	-18(1)
O(3)	10(2)	15(2)	7(2)	3(1)	-1(1)	-3(2)
Sr(1)	14(1)	25(1)	10(1)	0	0	0
O(4A)	40(3)	31(3)	27(3)	-3(2)	-8(2)	7(2)
O(4B)	62(3)	25(3)	23(3)	-1(2)	11(2)	0(2)

Table S3. Bond lengths [Å] and angles [deg] for $Sr_2Cu_5(PO_4)_4Cl_2 \cdot 8H_2O$.

Cu(1)-O(3)	1.932(3)	Sr(1)-O(3)#8	2.560(3)
Cu(1)-O(2)	1.941(3)	Sr(1)-O(3)#6	2.560(3)
Cu(1)-O(1)	1.956(3)	Sr(1)-O(5)#9	2.591(5)
Cu(1)-O(1)#1	1.968(3)	Sr(1)-O(6)#10	2.730(5)
Cu(1)-Cl(1)	2.709(2)	Sr(1)-O(6)#3	2.730(5)
P(1)-O(4)	1.515(3)	Sr(1)-O(2)#8	2.748(3)
P(1)-O(3)#5	1.531(3)	Sr(1)-O(2)#6	2.748(3)
P(1)-O(2)#6	1.544(3)	Sr(1)-O(5)	2.591(4)
P(1)-O(1)	1.553(3)	Cu(2)-O(4)#4	1.945(3)
Cu(2)-O(4)#3	1.945(3)	Cu(2)-O(4)	1.945(3)
Cu(2)-O(4)#1	1.945(3)	Cu(2)-Cl(2)	2.817(3)
O(3)-Cu(1)-O(2)	87.47(12)	O(4)#3-Cu(2)-O(4)#1	176.29(19)
O(3)-Cu(1)-O(1)	89.61(13)	O(4)#3-Cu(2)-O(4)#4	89.94(1)
O(2)-Cu(1)-O(1)	177.02(12)	O(4)#1-Cu(2)-O(4)#4	89.94(1)
O(3)-Cu(1)-O(1)#1	175.44(14)	O(4)#3-Cu(2)-O(4)	89.94(1)
O(2)-Cu(1)-O(1)#1	93.16(12)	O(4)#1-Cu(2)-O(4)	89.94(1)
O(1)-Cu(1)-O(1)#1	89.69(15)	O(4)#4-Cu(2)-O(4)	176.29(19)
O(3)-Cu(1)-Cl(1)	96.56(11)	O(4)#3-Cu(2)-Cl(2)	91.85(10)
O(2)-Cu(1)-Cl(1)	92.80(11)	O(4)#1-Cu(2)-Cl(2)	91.85(10)
O(1)-Cu(1)-Cl(1)	88.16(9)	O(4)#4-Cu(2)-Cl(2)	91.85(10)
O(1)#1-Cu(1)-Cl(1)	87.92(9)	O(4)-Cu(2)-Cl(2)	91.85(10)
O(4)-P(1)-O(3)#5	106.24(18)	O(5)#9-Sr(1)-O(6)#10	74.50(2)
O(4)-P(1)-O(2)#6	111.91(18)	O(5)#9-Sr(1)-O(6)#3	67.91(15)
O(3)#5-P(1)-O(2)#6	113.34(16)	O(5)#9-Sr(1)-O(2)#8	77.08(13)
O(4)-P(1)-O(1)	110.50(16)	O(5)#9-Sr(1)-O(2)#6	159.04(14)
O(3)#5-P(1)-O(1)	108.37(19)	O(6)#10-Sr(1)-O(6)#3	121.40(2)
O(2)#6-P(1)-O(1)	106.47(18)	O(6)#10-Sr(1)-O(2)#8	128.30(13)
O(3)#8-Sr(1)-O(3)#6	100.26(16)	O(6)#10-Sr(1)-O(2)#6	84.80(16)
O(3)#8-Sr(1)-O(5)#9	122.17(14)	O(6)#3-Sr(1)-O(2)#8	84.80(16)
O(3)#8-Sr(1)-O(6)#10	163.23(17)	O(6)#3-Sr(1)-O(2)#6	128.30(13)
O(3)#8-Sr(1)-O(6)#3	70.72(13)	O(2)#8-Sr(1)-O(2)#6	114.53(14)
O(3)#8-Sr(1)-O(2)#8	60.47(8)	O(5)-Sr(1)-O(3)#8	108.04(12)
O(3)#8-Sr(1)-O(2)#6	78.44(9)	O(5)-Sr(1)-O(3)#6	122.17(14)
O(3)#6-Sr(1)-O(5)#9	108.04(12)	O(5)-Sr(1)-O(5)#9	97.90(2)
O(3)#6-Sr(1)-O(6)#10	70.72(13)	O(5)-Sr(1)-O(6)#10	67.91(15)
O(3)#6-Sr(1)-O(2)#8	78.44(9)	O(5)-Sr(1)-O(2)#8	159.04(14)
O(3)#6-Sr(1)-O(2)#6	60.47(8)	O(5)-Sr(1)-O(2)#6	77.08(13)
O(3)#6-Sr(1)-O(6)#3	163.23(17)	O(5)-Sr(1)-O(6)#3	74.50(2)

Symmetry transformations used to generate equivalent atoms:

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

#4 -x+2,-y+1,z #5 y,x,-z+2 #6 -x+3/2,y+1/2,-z+2

#7 -x+3/2,y-1/2,-z+2 #8 x+1/2,-y+3/2,-z+2 #9 -x+2,-y+2,z

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

Table S4. Bond lengths [A] and angles [deg] for $Sr_2Cu_5(PO_4)_4Br_2 \cdot 8H_2O$.

Cu(1)-O(2)#1	1.938(2)	Sr(1)-O(4B)#15	2.587(5)
Cu(1)-O(2)	1.938(2)	Sr(1)-O(4B)#1	2.587(5)
Cu(1)-O(1)#2	1.961(2)	Sr(1)-O(4B)#9	2.587(5)
Cu(1)-O(1)#3	1.961(2)	Sr(1)-O(4B)	2.587(5)
Cu(1)-Br(1)	2.832(1)	Sr(1)-O(2)#9	2.649(2)
P(1)-O(2)#5	1.535(2)	Sr(1)-O(2)#15	2.649(2)
P(1)-O(2)	1.535(2)	Sr(1)-O(2)#1	2.649(2)
P(1)-O(3)	1.556(3)	Sr(1)-O(2)	2.649(2)
P(1)-O(1)	1.560(3)	Sr(1)-O(4A)#1	2.700(4)
Cu(2)-O(3)	1.946(3)	Sr(1)-O(4A)	2.700(4)
Cu(2)-O(3)#6	1.946(3)	Sr(1)-O(4A)#9	2.700(4)
Cu(2)-O(3)#7	1.946(3)	Sr(1)-O(4A)#15	2.700(4)
Cu(2)-O(3)#8	1.946(3)		
Cu(2)-Br(2)	2.964(2)		
O(2)#1-Cu(1)-O(2)	88.34(13)	O(3)-Cu(2)-O(3)#6	177.60(2)
O(2)#1-Cu(1)-O(1)#2	176.64(10)	O(3)-Cu(2)-O(3)#7	89.98(1)
O(2)-Cu(1)-O(1)#2	90.87(10)	O(3)#6-Cu(2)-O(3)#7	89.98(1)
O(2)#1-Cu(1)-O(1)#3	90.87(10)	O(3)-Cu(2)-O(3)#8	89.98(1)
O(2)-Cu(1)-O(1)#3	176.64(10)	O(3)#6-Cu(2)-O(3)#8	89.98(1)
O(1)#2-Cu(1)-O(1)#3	89.74(15)	O(3)#7-Cu(2)-O(3)#8	177.60(2)
O(2)#1-Cu(1)-Br(1)	93.00(7)	O(3)-Cu(2)-Br(2)	91.19(11)
O(2)-Cu(1)-Br(1)	93.00(7)	O(3)#6-Cu(2)-Br(2)	91.19(11)
O(1)#2-Cu(1)-Br(1)	90.30(7)	O(3)#7-Cu(2)-Br(2)	91.19(11)
O(1)#3-Cu(1)-Br(1)	90.30(7)	O(3)#8-Cu(2)-Br(2)	91.19(11)
O(2)#5-P(1)-O(2)	113.38(16)	O(4B)#1-Sr(1)-O(2)#15	77.78(12)
O(2)#5-P(1)-O(3)	96.58(13)	O(4B)#1-Sr(1)-O(4B)	83.30(2)
O(2)-P(1)-O(3)	121.09(15)	O(4B)#1-Sr(1)-O(4B)#9	100.70(2)
O(2)#5-P(1)-O(1)	107.60(10)	O(4B)#1-Sr(1)-O(2)#9	117.77(13)
O(2)-P(1)-O(1)	107.60(10)	O(4B)#1-Sr(1)-O(2)#1	106.20(12)
O(3)-P(1)-O(1)	109.70(16)	O(4B)#1-Sr(1)-O(4A)#1	72.60(17)
O(4B)#15-Sr(1)-O(4B)#1	45.70(2)	O(4B)#1-Sr(1)-O(4A)	100.95(15)
O(4B)#15-Sr(1)-O(4B)#9	83.30(2)	O(4B)#1-Sr(1)-O(4A)#9	66.70(15)
O(4B)#15-Sr(1)-O(2)#9	163.07(12)	O(4B)#1-Sr(1)-O(4A)#15	27.81(15)
O(4B)#15-Sr(1)-O(4B)	100.70(2)	O(4B)#9-Sr(1)-O(2)#9	106.20(12)
O(4B)#15-Sr(1)-O(2)#15	106.20(11)	O(4B)#9-Sr(1)-O(4B)	45.70(2)
O(4B)#15-Sr(1)-O(2)#1	77.78(12)	O(4B)#9-Sr(1)-O(2)#15	163.07(12)
O(4B)#15-Sr(1)-O(4A)#15	72.60(17)	O(4B)#9-Sr(1)-O(2)#1	117.77(13)
O(4B)#15-Sr(1)-O(4A)#1	27.81(15)	O(4B)#9-Sr(1)-O(4A)#1	66.70(15)
O(4B)#15-Sr(1)-O(4A)	66.70(15)	O(4B)#9-Sr(1)-O(4A)	27.81(15)
O(4B)#15-Sr(1)-O(4A)#9	100.95(15)	O(4B)#9-Sr(1)-O(4A)#9	72.60(17)
O(4B)-Sr(1)-O(2)#9	77.78(12)	O(4B)#9-Sr(1)-O(4A)#15	100.95(15)
O(4B)-Sr(1)-O(2)#1	163.07(12)	O(2)#9-Sr(1)-O(2)#15	61.27(8)

O(4B)-Sr(1)-O(4A)#1	100.95(15)	O(2)#9-Sr(1)-O(2)#1	108.60(10)
O(4B)-Sr(1)-O(2)#15	117.77(13)	O(2)#9-Sr(1)-O(4A)	127.37(11)
O(4B)-Sr(1)-O(4A)	72.60(17)	O(2)#9-Sr(1)-O(4A)#1	169.03(11)
O(4B)-Sr(1)-O(4A)#9	27.81(15)	O(2)#9-Sr(1)-O(4A)#9	69.72(12)
O(4B)-Sr(1)-O(4A)#15	66.70(15)	O(2)#9-Sr(1)-O(4A)#15	91.61(12)
O(2)#15-Sr(1)-O(2)#1	78.44(8)	O(2)#1-Sr(1)-O(4A)#1	69.72(12)
O(2)#15-Sr(1)-O(4A)#1	127.37(11)	O(2)#1-Sr(1)-O(4A)	91.61(12)
O(2)#15-Sr(1)-O(4A)	169.04(11)	O(2)#1-Sr(1)-O(4A)#9	169.04(11)
O(2)#15-Sr(1)-O(4A)#9	91.61(12)	O(2)#1-Sr(1)-O(4A)#15	127.37(11)
O(2)#15-Sr(1)-O(4A)#15	69.72(12)	O(4A)-Sr(1)-O(4A)#9	97.90(2)
O(4A)#1-Sr(1)-O(4A)	43.20(2)	O(4A)-Sr(1)-O(4A)#15	114.10(2)
O(4A)#1-Sr(1)-O(4A)#9	114.10(2)	O(4A)#9-Sr(1)-O(4A)#15	43.20(2)
O(4A)#1-Sr(1)-O(4A)#15	97.90(2)	O(2)-Sr(1)-O(2)#1	61.27(8)
O(2)-Sr(1)-O(4B)#15	117.77(13)	O(2)-Sr(1)-O(4A)#1	91.61(12)
O(2)-Sr(1)-O(4B)#1	163.07(12)	O(2)-Sr(1)-O(4A)	69.72(12)
O(2)-Sr(1)-O(4B)#9	77.78(12)	O(2)-Sr(1)-O(4A)#9	127.37(11)
O(2)-Sr(1)-O(4B)	106.20(11)	O(2)-Sr(1)-O(4A)#15	169.03(11)
O(2)-Sr(1)-O(2)#9	78.44(8)	O(2)-Sr(1)-O(2)#15	108.60(10)

Symmetry transformations used to generate equivalent atoms:

#1 x,-y+3/2,z	#2 -x+1,-y+1,-z	#3 -y+1,x+1/2,-z
#4 -y+1/2,-x+1/2,z	#5 y,x,z	#6 -x+1/2,-y+1/2,z
#7 y,-x+1/2,z	#8 -y+1/2,x,z	#9 -x+1/2,y,z
#10 x,-y+1/2,z	#11 -y+3/2,x,z	#12 y,-x+3/2,z
#13 -x+3/2,-y+3/2,z	#14 y-1/2,-x+1,-z	#15 -x+1/2,-y+3/2,z