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Supporting Information

Alkaline Earth Metal Zirconate Perovskites $MZrO_3$ ($M = Ba^{2+}$, Sr^{2+}, Ca^{2+}) Derived from Molecular Precursors and Doped with Eu^{3+} Ions

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Supporting Information

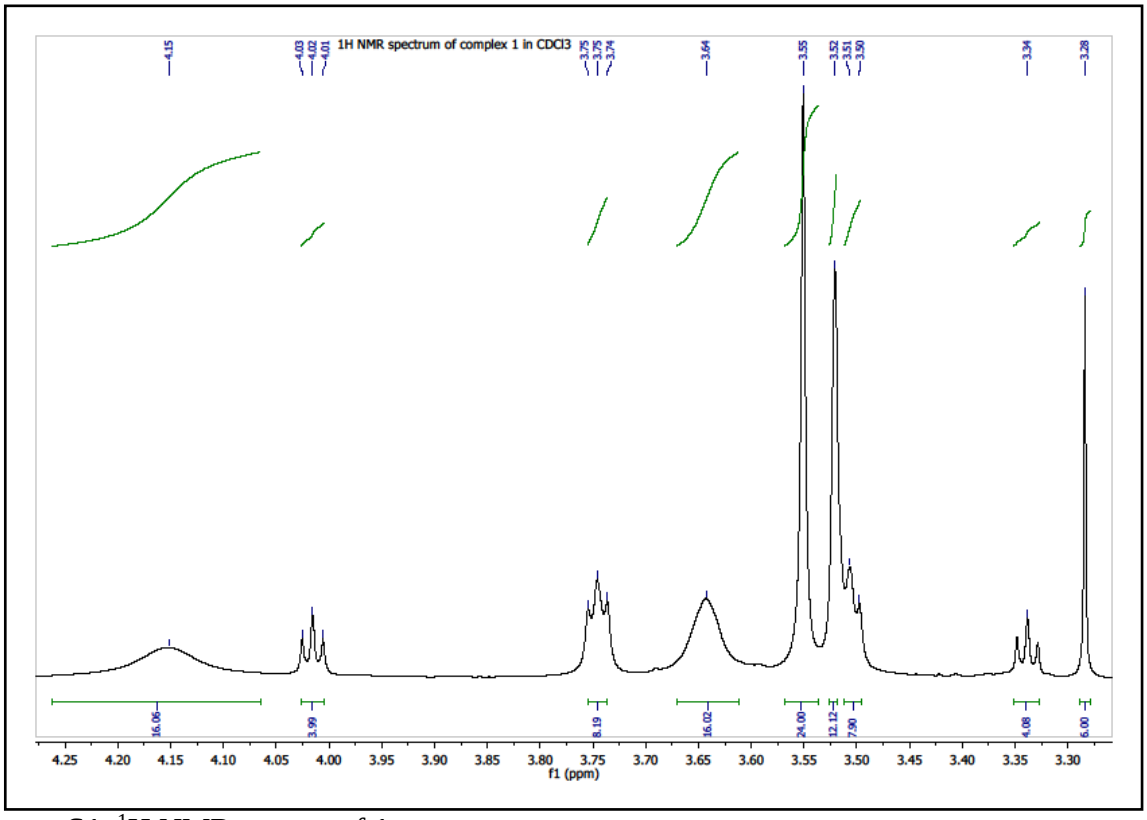

Figure S1. ^{1}H NMR spectra of **1**.

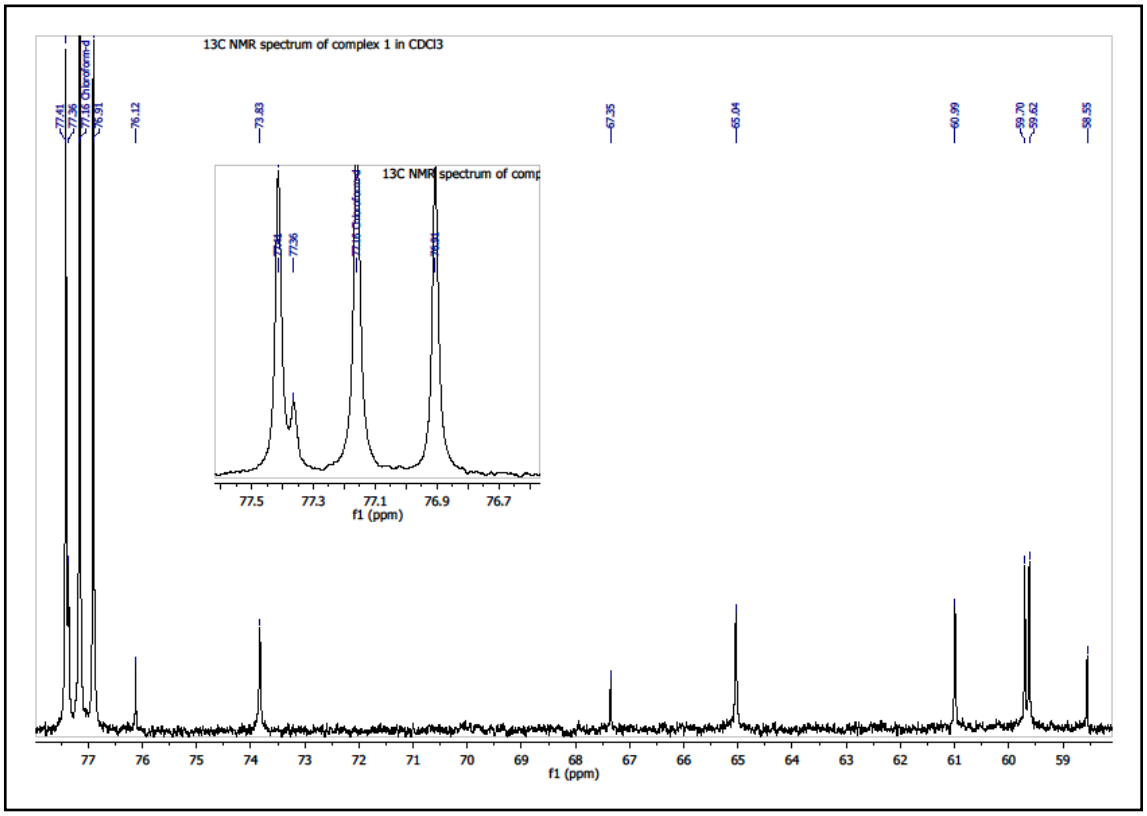

Figure S2. ^{13}C NMR spectra of **1**.

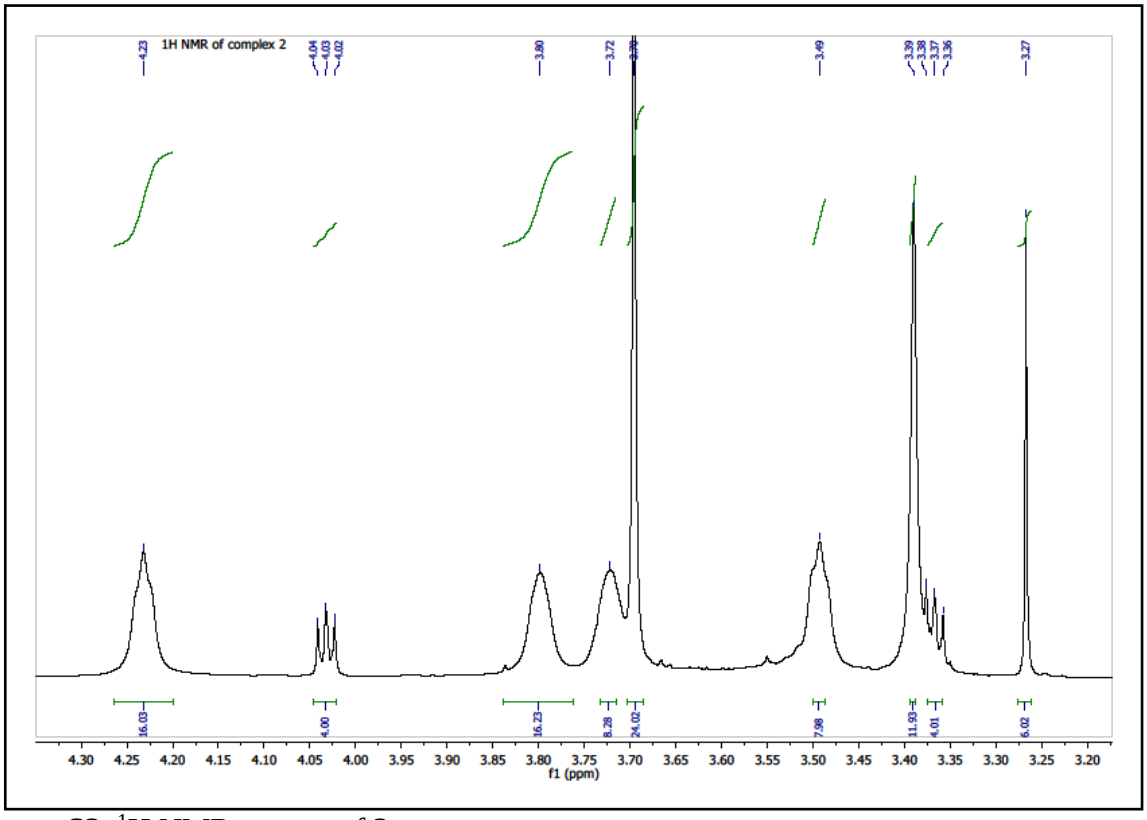

Figure S3. ^{1}H NMR spectra of **2**.

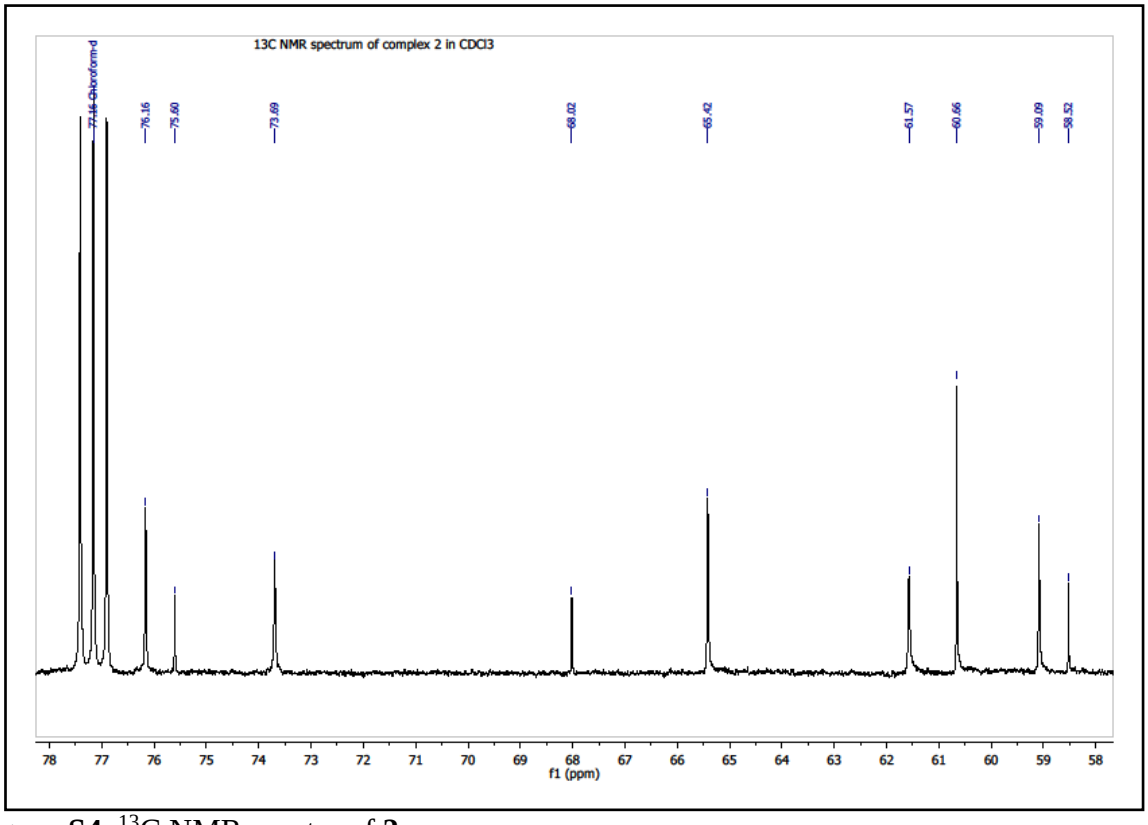

Figure S4. ^{13}C NMR spectra of **2**.

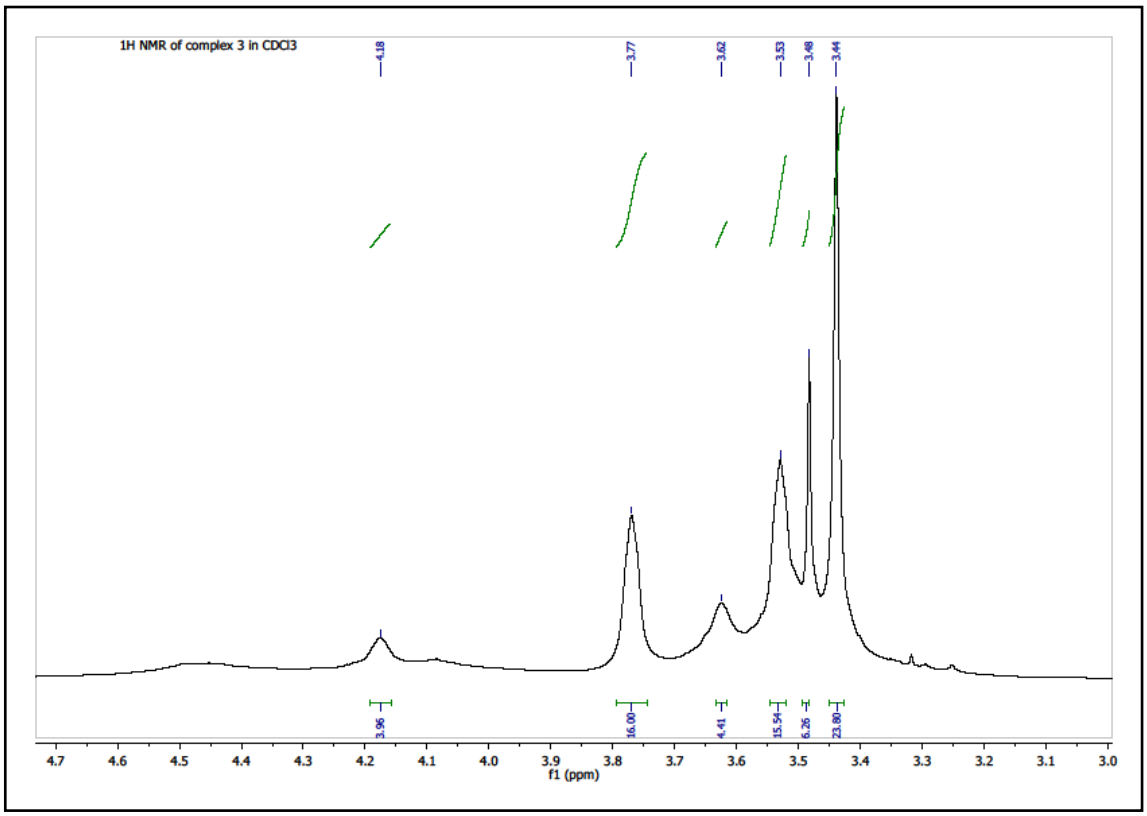

Figure S5. ^{1}H NMR spectra of **3**.

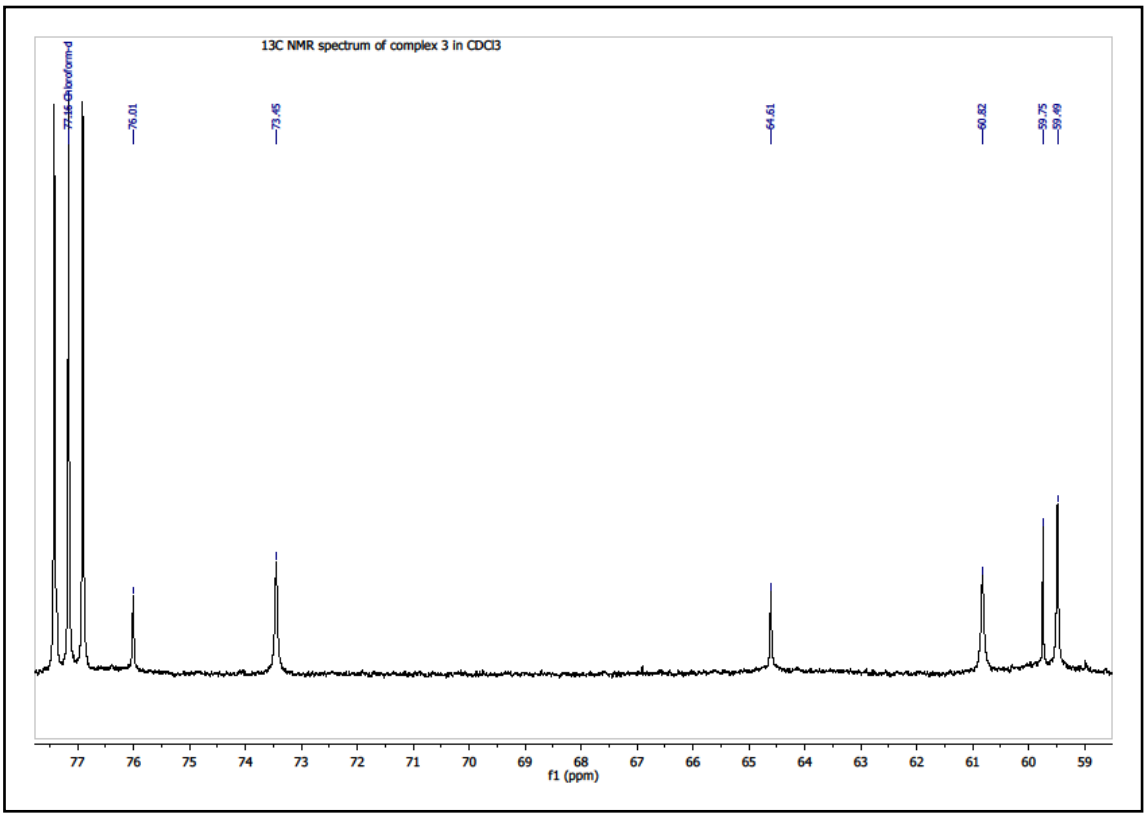

Figure S6. ^{13}C NMR spectra of **3**.

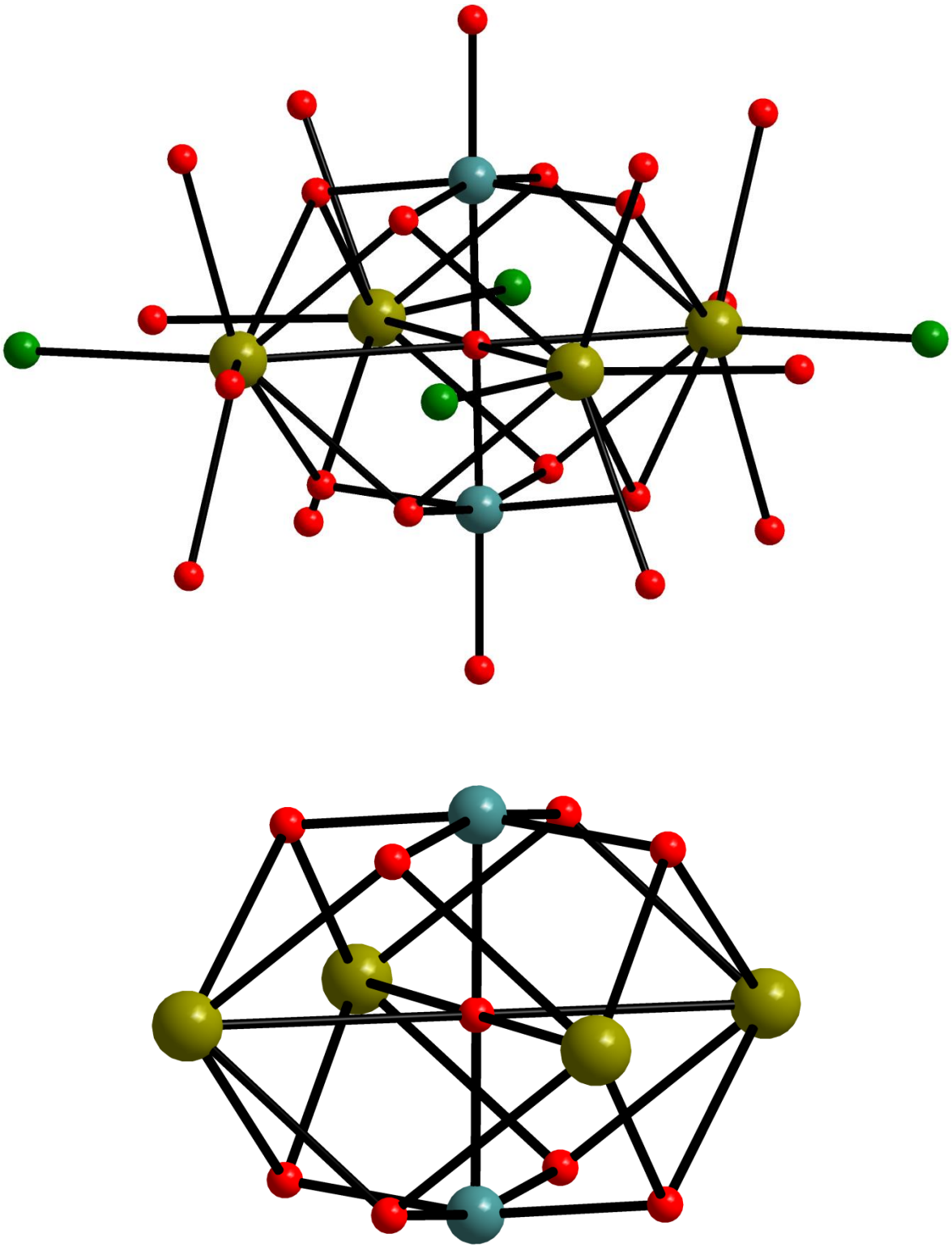

Figure S7. Central $Ba_4Zr_2(\mu_6\text{-}O)(\mu_3\text{-}O)_8$ core geometry.

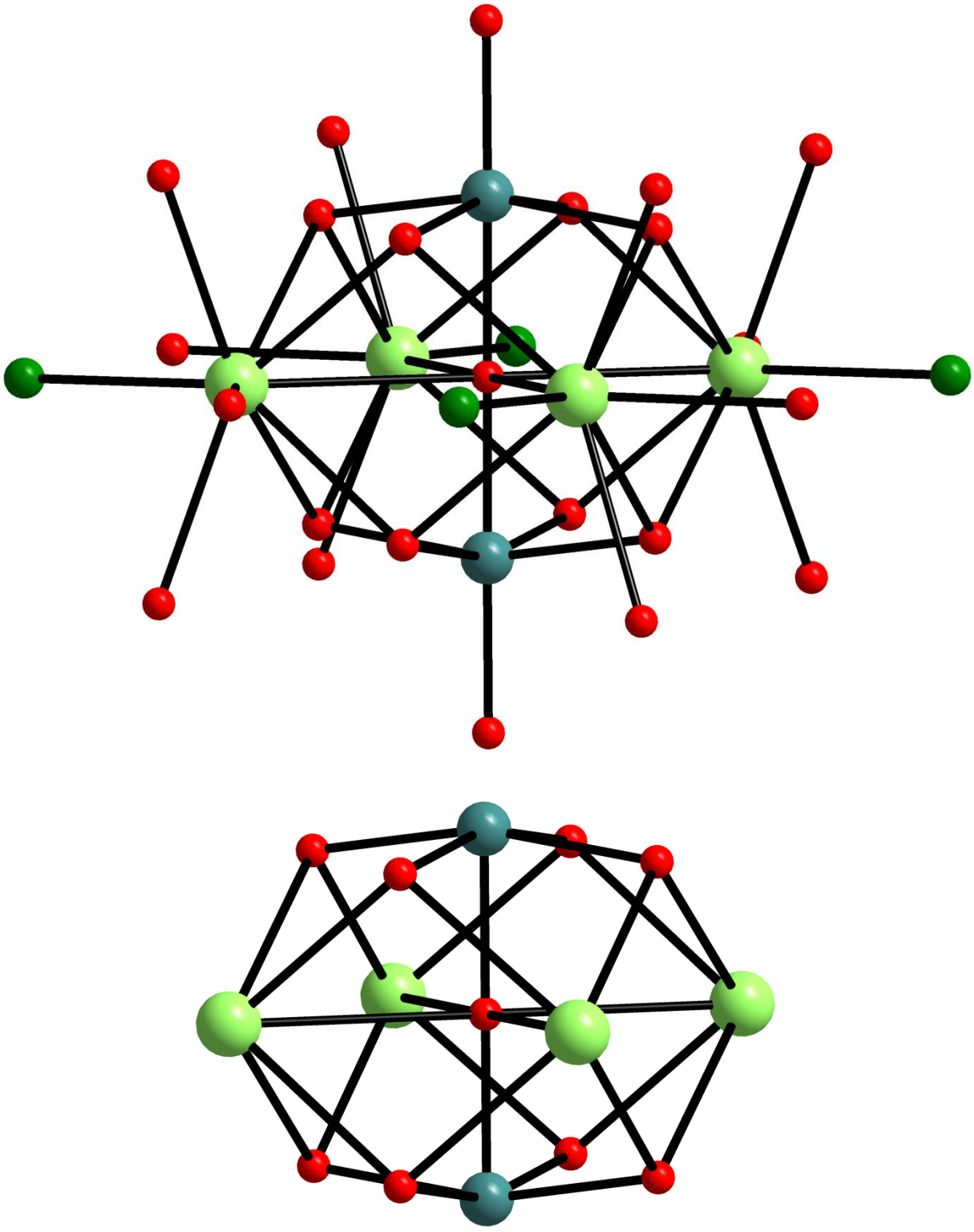

Figure S8. Central $Sr_4Zr_2(\mu_6\text{-}O)(\mu_3\text{-}O)_8$ core geometry.

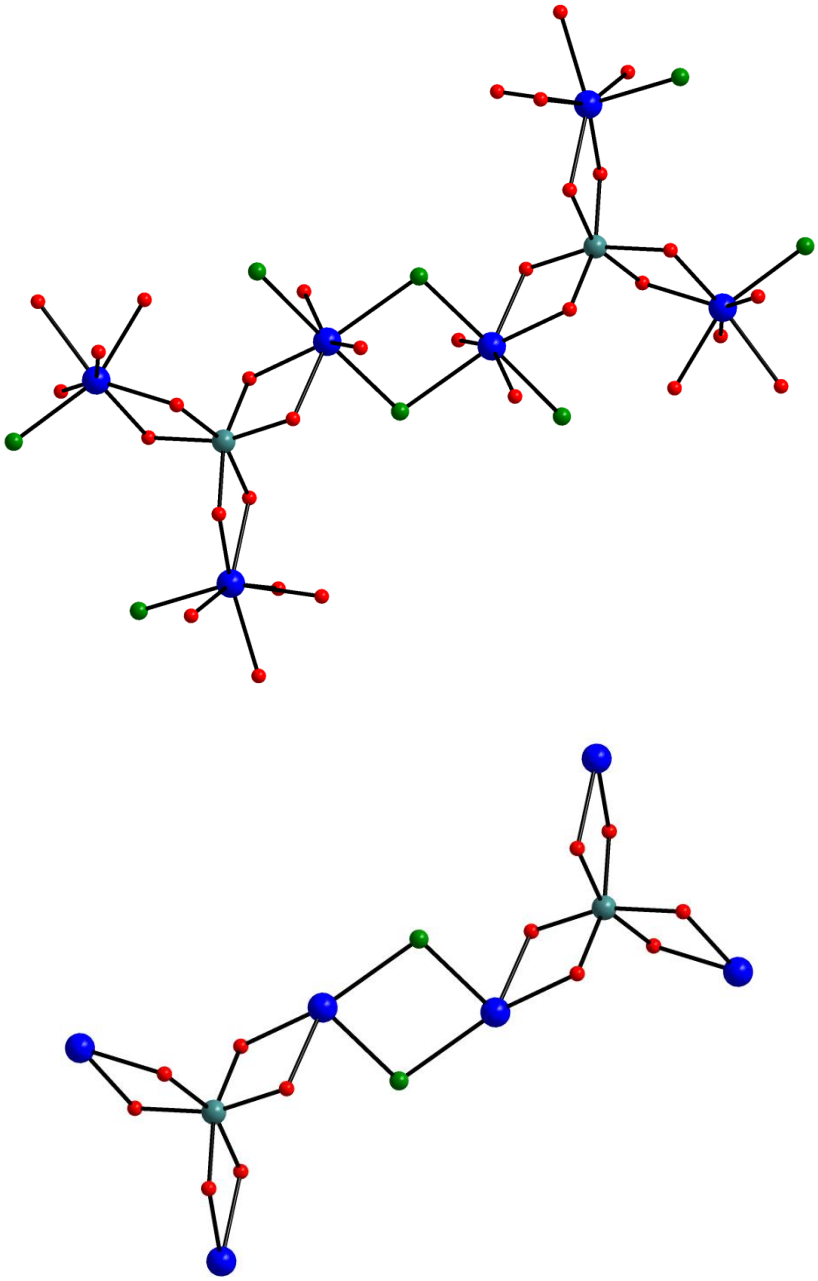

Figure S9. Central $Ca_6Zr_2(\mu_2\text{-}O)_{12}(\mu_2\text{-}Cl)_2$ core geometry.

Crystallography. XRD data were collected at 100 K using a KUMA KM4 CCD κ-geometry diffractometer (ω scan technique).[1] The experimental details and the crystal data are given in Table S1(SI). The structures were solved by direct methods and refined by full-matrix least-squares on F^2 using the *SHELXTL* package.[2] Non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were positioned geometrically and added to the structure factor calculations, but were not refined. The molecular graphics were created using Diamond, version 3.1e.[3] Crystallographic data for the structural analyses reported in this paper have also been deposited with the Cambridge Crystallographic Data Centre (CCDC), number 1435943-1435947. Copies of the information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk; home page: http://www.ccdc.cam.ac.uk).

Crystallographic Data for Compounds 1, 2 and 4.

Table S2. Crystal and Data Collection Parameters for Compounds **1**, **2** and **4**.

	1	**1'**	**1"** ·2 EtOH	**2**	**4**·8 CH_2Cl_2
Chemical formula	$C_{42}H_{102}Ba_4Cl_4O_{29}Zr_2$	$C_{42}H_{102}Ba_4Cl_4O_{29}Zr_2$	$C_{45}H_{112}Ba_4Cl_4O_{30}Zr_2$	$C_{42}H_{102}Cl_4O_{29}Sr_4Zr_2$	$C_{56}H_{132}Ca_6Cl_{24}O_{32}Zr_2$
Formula Mass	1944.80	1944.80	2006.91	1745.95	2591.33
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic	Triclinic
Space group	*P*$\bar{1}$	*P*$\bar{1}$	*P*$\bar{1}$	*P*$\bar{1}$	*P*$\bar{1}$
a/Å	12.793(6)	12.669(2)	12.548(3)	12.177(4)	13.655(3)
b/Å	12.957(6)	12.860(3)	12.861(3)	12.857(5)	14.289(3)
c/Å	13.325(4)	13.512(2)	13.129(4)	13.226(4)	16.242(4)
α/°	88.94(2)	106.74(2)	117.34(3)	64.97(3)	93.92
β/°	68.82(2)	103.73(2)	99.64(2)	75.27(2)	112.47
γ/°	63.85(2)	113.55(3)	92.38(2)	66.34(3)	100.39
Unit cell volume/Å^3	1822.4(14)	1770.0(10)	1838.5(10)	1709.6(11)	2847.4(12)
Temperature/K	100(2)	100(2)	100(2)	100(2)	100(2)
Z	1	1	1	1	1
Radiation type	MoKα	MoKα	MoKα	MoKα	MoKα
Absorption coefficient, μ/mm^{-1}	2.620	2.697	2.601	3.623	1.079
No. of reflections measured	23087	24829	13755	15170	35476
No. of independent reflections	7940	7718	7881	7415	18280
No. of observed reflections ($I > 2\sigma(I)$)	7070	6648	6691	5536	11911
R_{int}	0.0339	0.0236	0.0352	0.0597	0.0363
Final R_1 values ($I > 2\sigma(I)$)	0.0296	0.0220	0.0470	0.0487	0.0482
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.0806	0.0532	0.1319	0.1198	0.1199
Final R_1 values (all data)	0.0333	0.0287	0.0544	0.0658	0.0824
Final $wR(F^2)$ values (all data)	0.0823	0.0550	0.1371	0.1251	0.1331
Goodness of fit on F^2	1.046	1.045	1.091	0.953	0.968
Δρmax/eÅ^{-3}	0.81	1.44	1.55	0.76	0.80
Δρmin/eÅ^{-3}	-0.78	-0.39	-1.24	-0.99	-0.76

Table S2. Seleceted geometric parameters for **1-3** (Å, °).

1		**2**	
Ba1—O1	3.155(2)	Sr1—O1	2.991(2)
Ba1—O2	2.816(2)	Sr1—O2	2.671(3)
Ba1—O3	2.784(2)	Sr1—O3	2.626(3)
Ba1—O4	2.843(2)	Sr1—O4	2.667(3)
Ba1—O5	2.776(2)	Sr1—O5	2.650(3)
Ba1—O6^i	2.920(2)	Sr1—O6^i	2.780(3)
Ba1—O8^i	2.919(2)	Sr1—O8^i	2.809(3)
Ba1—O10	2.732(3)	Sr1—O10	2.621(3)
Ba1—O11	3.316(3)	Sr1—O11	3.255(4)
Ba1—Cl1	3.097(2)	Sr1—Cl1	2.905(3)
Ba2—O1	3.151(2)	Sr2—O1	2.898(2)

Ba2—O2	2.906(2)	Sr2—O2	2.682(3)
Ba2—O4	2.927(2)	Sr2—O4	2.743(3)
Ba2—O6	2.813(2)	Sr2—O6	2.631(3)
Ba2—O7	2.813(3)	Sr2—O7	2.709(3)
Ba2—O8	2.812(2)	Sr2—O8	2.627(3)
Ba2—O9	2.790(2)	Sr2—O9	2.726(3)
Ba2—O12	2.750(3)	Sr2—O12	2.541(4)
Ba2—O13	3.196(3)		
Ba2—Cl2	3.065(2)	Sr2—Cl2	2.907(2)
Zr1—O1	2.0329(6)	Zr1—O1	2.0252(7)
Zr1—O2	2.121(2)	Zr1—O2	2.140(3)
Zr1—O4^{i}	2.124(2)	Zr1—O4^{i}	2.115(3)
Zr1—O6	2.129(2)	Zr1—O6	2.124(3)
Zr1—O8^{i}	2.119(2)	Zr1—O8^{i}	2.118(3)
Zr1—O14	1.985(2)	Zr1—O14	1.968(3)
O1—Ba1—O11	168.47(5)	O1—Sr1—Cl1	124.02(4)
O1—Ba1—Cl1	126.51(3)	O1—Sr1—O11	167.09(7)
O2—Ba1—O1	54.69(5)	O2—Sr1—O1	56.68(7)
O2—Ba1—O4	78.96(6)	O2—Sr1—O4	79.79(10)
O2—Ba1—O6^{i}	108.88(6)	O2—Sr1—O6^{i}	112.75(9)
O2—Ba1—O8^{i}	62.88(6)	O2—Sr1—O8^{i}	66.43(9)
O2—Ba1—O11	117.51(7)	O2—Sr1—O11	113.85(10)
O2—Ba1—Cl1	139.86(5)	O2—Sr1—Cl1	140.45(8)
O3—Ba1—O1	108.77(5)	O3—Sr1—O1	112.62(8)
O3—Ba1—O2	60.51(7)	O3—Sr1—O2	63.56(10)
O3—Ba1—O4	133.63(7)	O3—Sr1—O4	136.28(10)
O3—Ba1—O6^{i}	148.78(7)	O3—Sr1—O6^{i}	149.24(10)
O3—Ba1—O8^{i}	72.80(7)	O3—Sr1—O8^{i}	74.52(10)
O3—Ba1—O11	69.39(8)	O3—Sr1—O11	65.10(11)
O3—Ba1—Cl1	87.55(6)	O3—Sr1—Cl1	85.56(8)
O4—Ba1—O1	55.05(5)	O4—Sr1—O1	57.20(7)
O4—Ba1—O6^{i}	62.52(6)	O4—Sr1—O6^{i}	65.83(10)
O4—Ba1—O8^{i}	109.35(6)	O4—Sr1—O8^{i}	112.98(9)
O4—Ba1—O11	117.39(7)	O4—Sr1—O11	114.76(10)
O4—Ba1—Cl1	138.33(5)	O4—Sr1—Cl1	137.14(8)
O5—Ba1—O1	109.75(5)	O5—Sr1—O1	113.98(8)
O5—Ba1—O2	131.85(7)	O5—Sr1—O2	135.61(10)
O5—Ba1—O3	135.12(7)	O5—Sr1—O3	130.12(10)
O5—Ba1—O4	59.96(7)	O5—Sr1—O4	63.66(10)
O5—Ba1—O6^{i}	74.95(7)	O5—Sr1—O6^{i}	75.49(10)
O5—Ba1—O8^{i}	151.01(7)	O5—Sr1—O8^{i}	150.00(10)
O5—Ba1—O11	68.21(8)	O5—Sr1—O11	65.46(11)
O5—Ba1—Cl1	87.65(6)	O5—Sr1—Cl1	82.93(8)
O6^{i}—Ba1—O1	54.20(5)	O6^{i}—Sr1—O1	56.08(7)

O6^{i}—Ba1—O11	132.79(7)	O6^{i}—Sr1—O11	132.56(10)
O6^{i}—Ba1—Cl1	85.44(5)	O6^{i}—Sr1—Cl1	80.94(7)
O8^{i}—Ba1—O1	54.32(4)	O8^{i}—Sr1—O1	55.82(7)
O8^{i}—Ba1—O6^{i}	76.38(6)	O8^{i}—Sr1—O6^{i}	76.39(9)
O8^{i}—Ba1—O11	132.50(7)	O8^{i}—Sr1—O11	131.38(10)
O8^{i}—Ba1—Cl1	85.94(6)	O8^{i}—Sr1—Cl1	82.53(7)
O10—Ba1—O1	114.44(6)	O10—Sr1—O1	112.25(8)
O10—Ba1—O2	76.21(7)	O10—Sr1—O2	73.04(10)
O10—Ba1—O3	72.36(8)	O10—Sr1—O3	74.13(11)
O10—Ba1—O4	77.17(8)	O10—Sr1—O4	72.92(10)
O10—Ba1—O5	71.36(8)	O10—Sr1—O5	72.77(11)
O10—Ba1—O6^{i}	136.65(7)	O10—Sr1—O6^{i}	135.90(10)
O10—Ba1—O8^{i}	135.53(7)	O10—Sr1—O8^{i}	136.61(10)
O10—Ba1—O11	54.03(8)	O10—Sr1—O11	54.88(11)
O10—Ba1—Cl1	119.06(6)	O10—Sr1—Cl1	123.71(8)
O11—Ba1—Cl1	65.02(6)	O11—Sr1—Cl1	68.89(8)
O1—Ba2—O13	167.30(5)		
O1—Ba2—Cl2	124.36(4)	O1—Sr2—Cl2	132.77(4)
O2—Ba2—O1	54.02(5)	O2—Sr2—O1	57.77(7)
O2—Ba2—O4	76.17(6)	O2—Sr2—O4	78.23(10)
O2—Ba2—O13	132.36(7)		
O2—Ba2—Cl2	84.40(6)	O2—Sr2—Cl2	86.09(8)
O4—Ba2—O1	54.41(5)	O4—Sr2—O1	57.65(7)
O4—Ba2—O13	134.22(8)		
O4—Ba2—Cl2	83.55(5)	O4—Sr2—Cl2	88.18(7)
O6—Ba2—O1	55.11(5)	O6—Sr2—O1	58.68(7)
O6—Ba2—O2	62.69(6)	O6—Sr2—O2	67.82(10)
O6—Ba2—O4	109.51(6)	O6—Sr2—O4	116.31(10)
O6—Ba2—O13	115.52(8)		
O6—Ba2—Cl2	138.80(5)	O6—Sr2—Cl2	137.76(7)
O7—Ba2—O1	109.92(6)	O7—Sr2—O1	116.27(8)
O7—Ba2—O2	74.97(7)	O7—Sr2—O2	77.77(10)
O7—Ba2—O4	150.74(7)	O7—Sr2—O4	153.52(10)
O7—Ba2—O6	60.31(7)	O7—Sr2—O6	63.58(10)
O7—Ba2—O13	66.57(9)		
O7—Ba2—Cl2	88.89(6)	O7—Sr2—Cl2	79.21(8)
O8—Ba2—O1	55.24(5)	O8—Sr2—O1	58.73(7)
O8—Ba2—O2	109.23(6)	O8—Sr2—O2	116.45(10)
O8—Ba2—O4	62.52(6)	O8—Sr2—O4	66.91(9)
O8—Ba2—O6	79.85(6)	O8—Sr2—O6	82.19(10)
O8—Ba2—O7	133.15(7)	O8—Sr2—O7	135.22(10)
O8—Ba2—O13	117.37(7)		
O8—Ba2—Cl2	137.50(5)	O8—Sr2—Cl2	140.05(7)
O9—Ba2—O1	110.06(6)	O9—Sr2—O1	114.66(7)

O9—Ba2—O2	150.28(7)	O9—Sr2—O2	149.21(10)
O9—Ba2—O4	74.50(7)	O9—Sr2—O4	73.93(10)
O9—Ba2—O6	133.20(7)	O9—Sr2—O6	137.49(10)
O9—Ba2—O7	133.53(8)	O9—Sr2—O7	125.63(10)
O9—Ba2—O8	60.32(7)	O9—Sr2—O8	63.54(10)
O9—Ba2—O13	69.18(8)		
O9—Ba2—Cl2	87.61(6)	O9—Sr2—Cl2	80.21(8)
O12—Ba2—O1	113.02(6)	O12—Sr2—O1	119.59(8)
O12—Ba2—O2	136.07(7)	O12—Sr2—O2	140.50(11)
O12—Ba2—O4	134.98(8)	O12—Sr2—O4	137.23(11)
O12—Ba2—O6	75.95(8)	O12—Sr2—O6	78.23(11)
O12—Ba2—O7	72.06(9)	O12—Sr2—O7	69.19(11)
O12—Ba2—O8	75.35(8)	O12—Sr2—O8	76.55(10)
O12—Ba2—O9	71.25(8)	O12—Sr2—O9	70.26(11)
O12—Ba2—O13	54.38(8)		
O12—Ba2—Cl2	122.61(6)	O12—Sr2—Cl2	107.64(9)
O13—Ba2—Cl2	68.29(6)		
O1—Zr1—O2	83.22(6)	O1—Zr1—O2	80.84(9)
O1—Zr1—O4^{i}	84.12(6)	O1—Zr1—O4^{i}	82.21(9)
O1—Zr1—O6	83.62(7)	O1—Zr1—O6	81.86(9)
O1—Zr1—O8^{i}	84.06(6)	O1—Zr1—O8^{i}	82.02(9)
O2—Zr1—O4^{i}	167.34(8)	O2—Zr1—O4^{i}	163.03(12)
O2—Zr1—O6	88.91(9)	O2—Zr1—O6	88.10(12)
O4^{i}—Zr1—O6	89.39(8)	O4^{i}—Zr1—O6	88.62(12)
O8^{i}—Zr1—O2	89.79(8)	O8^{i}—Zr1—O2	89.74(12)
O8^{i}—Zr1—O4^{i}	89.21(8)	O8^{i}—Zr1—O4^{i}	88.81(12)
O8^{i}—Zr1—O6	167.68(9)	O8^{i}—Zr1—O6	163.88(12)
O14—Zr1—O1	178.40(7)	O14—Zr1—O1	177.10(9)
O14—Zr1—O2	96.24(9)	O14—Zr1—O2	96.39(12)
O14—Zr1—O4^{i}	96.41(9)	O14—Zr1—O4^{i}	100.54(13)
O14—Zr1—O6	94.88(9)	O14—Zr1—O6	97.24(13)
O14—Zr1—O8^{i}	97.44(9)	O14—Zr1—O8^{i}	98.87(13)
Ba1—O1—Ba1^{i}	180.0	Sr1—O1—Sr1^{i}	180.0
Ba1—O2—Ba2	102.85(7)	Sr1—O2—Sr2	101.73(11)
Ba1—O4—Ba2	101.65(7)	Sr1—O4—Sr2	100.25(11)
Ba2—O1—Ba1	90.37(3)	Sr2—O1—Sr1	89.66(4)
Ba2—O1—Ba1^{i}	89.63(3)	Sr2—O1—Sr1^{i}	90.34(4)
Ba2^{i}—O1—Ba2	180.0	Sr2^{i}—O1—Sr2	180.0
Ba2—O6—Ba1^{i}	101.64(7)	Sr2—O6—Sr1^{i}	101.02(10)
Ba2—O8—Ba1^{i}	101.68(7)	Sr2—O8—Sr1^{i}	100.39(10)
Zr1—O1—Ba1	89.78(3)	Zr1—O1—Sr1	90.20(3)
Zr1—O1—Ba1^{i}	90.22(3)	Zr1—O1—Sr1^{i}	89.80(3)
Zr1—O1—Ba2	90.12(4)	Zr1—O1—Sr2	89.97(4)
Zr1—O1—Ba2^{i}	89.88(4)	Zr1—O1—Sr2^{i}	90.03(3)

Zr1—O2—Ba1	97.75(8)	Zr1—O2—Sr1	96.92(11)
Zr1—O2—Ba2	95.33(8)	Zr1—O2—Sr2	93.58(11)
Zr1^{i}—O4—Ba1	97.33 (8)	Zr1^{i}—O4—Sr1	97.22(12)
Zr1^{i}—O4—Ba2	94.41 (7)	Zr1^{i}—O4—Sr2	92.48(11)
Zr1—O6—Ba1^{i}	95.00(8)	Zr1—O6—Sr1^{i}	93.72(11)
Zr1—O6—Ba2	97.89(8)	Zr1—O6—Sr2	95.44(12)
Zr1^{i}—O8—Ba1^{i}	94.75 (8)	Zr1^{i}—O8—Sr1^{i}	93.46(11)
Zr1^{i}—O8—Ba2	97.88 (8)	Zr1^{i}—O8—Sr2	95.79(11)
Zr1^{i}—O1—Zr1	180.0	Zr1^{i}—O1—Zr1	180.0
		4	
Ca1—O1	2.394(2)	Ca3—O11	2.347(2)
Ca1—O2A	2.449(7)	Ca3—O12	2.489(2)
Ca1—O3	2.399(2)	Ca3—O13A	2.422(7)
Ca1—O4	2.473(2)	Ca3—O14A	2.461(6)
Ca1—Cl1	2.831(2)	Ca3—O15	2.355(2)
Ca1—Cl1^{i}	2.749(2)	Ca3—O16A	2.485(8)
Ca1—Cl2A	2.792(7)	Ca3—Cl4	2.694(2)
Ca2—O5	2.346(2)	Zr1—O1	2.083(2)
Ca2—O6	2.541(2)	Zr1—O3	2.060(2)
Ca2—O7	2.386(2)	Zr1—O5	2.089(2)
Ca2—O8	2.458(2)	Zr1—O9	2.077(2)
Ca2—O9	2.351(2)	Zr1—O11	2.090(2)
Ca2—O10	2.524(2)	Zr1—O15	2.083(2)
Ca2—Cl3	2.657(2)		
O1—Ca1—O2A	69.49(16)	O5—Ca2—O6	66.92(6)
O1—Ca1—O3	66.24(6)	O5—Ca2—O7	98.32(7)
O1—Ca1—O4	130.93(6)	O5—Ca2—O8	143.80(7)
O1—Ca1—Cl1	149.19(5)	O5—Ca2—O9	66.66(6)
O1—Ca1—Cl1^{i}	97.29(5)	O5—Ca2—O10	134.04(6)
O1—Ca1—Cl2A	85.65(17)	O5—Ca2—Cl3	102.18(5)
O2A—Ca1—O4	152.42(14)	O6—Ca2—Cl3	83.35(5)
O2A—Ca1—Cl1	80.95(16)	O7—Ca2—O6	96.76(7)
O2A—Ca1—Cl1^{i}	99.35(16)	O7—Ca2—O8	67.47(7)
O2A—Ca1—Cl2A	84.1(3)	O7—Ca2—O10	84.68(8)
O3—Ca1—O2A	135.69(16)	O7—Ca2—Cl3	157.67(6)
O3—Ca1—O4	68.32(6)	O8—Ca2—O6	81.40(7)
O3—Ca1—Cl1	142.11(4)	O8—Ca2—O10	79.57(7)
O3—Ca1—Cl1^{i}	84.70(5)	O8—Ca2—Cl3	90.58(5)
O3—Ca1—Cl2A	94.12(16)	O9—Ca2—O6	132.82(6)
O4—Ca1—Cl1	79.81(5)	O9—Ca2—O7	81.99(7)
O4—Ca1—Cl1^{i}	96.04(5)	O9—Ca2—O8	137.51(6)
O4—Ca1—Cl2A	80.0 (2)	O9—Ca2—O10	68.45(6)
Cl1^{i}—Ca1—Cl1	78.65(3)	O9—Ca2—Cl3	114.29(5)

Cl1^{i}—Ca1—Cl2A	176.0(2)	O10—Ca2—O6	158.72(6)
Cl2A—Ca1—Cl1	100.17(13)	O10—Ca2—Cl3	87.40(6)
O11—Ca3—O12	68.09(6)	O1—Zr1—O5	89.88(7)
O11—Ca3—O13A	137.88(15)	O1—Zr1—O11	163.13(7)
O11—Ca3—O14A	89.04(16)	O1—Zr1—O15	92.10(7)
O11—Ca3—O15	65.48(6)	O3—Zr1—O1	78.43(7)
O11—Ca3—O16A	132.56(18)	O3—Zr1—O9	92.16(7)
O11—Ca3—Cl4	112.02(5)	O3—Zr1—O11	93.67(7)
O12—Ca3—Cl4	87.61(6)	O3—Zr1—O15	103.45(7)
O13A—Ca3—O12	78.2(2)	O5—Zr1—O11	101.17(7)
O13A—Ca3—O14A	66.7(2)	O9—Zr1—O1	104.23(7)
O13A—Ca3—O16A	79.6(2)	O9—Zr1—O5	76.52(7)
O13A—Ca3—Cl4	90.37(16)	O9—Zr1—O11	90.83(7)
O14A—Ca3—O12	91.4(2)	O9—Zr1—O15	159.44(6)
O14A—Ca3—O16A	81.9(2)	O15—Zr1—O5	91.35(7)
O14A—Ca3—Cl4	156.69(16)	O15—Zr1—O11	75.09(7)
O15—Ca3—O12	133.15(6)	Zr1—O1—Ca1	107.24(7)
O15—Ca3—O13A	145.1(2)	Zr1—O3—Ca1	107.83(7)
O15—Ca3—O14A	93.7(2)	Zr1—O5—Ca2	107.01(7)
O15—Ca3—O16A	68.78(17)	Zr1—O9—Ca2	107.25(7)
O15—Ca3—Cl4	103.88(5)	Zr1—O11—Ca3	108.88(8)
O16A—Ca3—O12	157.71(17)	Zr1—O15—Ca3	108.78(8)
O16A—Ca3—Cl4	90.28(14)		

Symmetry codes:(i) −x+1, −y+1, −z+1.

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