

Multiple dimensionalities in the $A_2M_3(SO_4)_4$ ($A = Rb, Cs$ $M = Co, Ni$) analogues.

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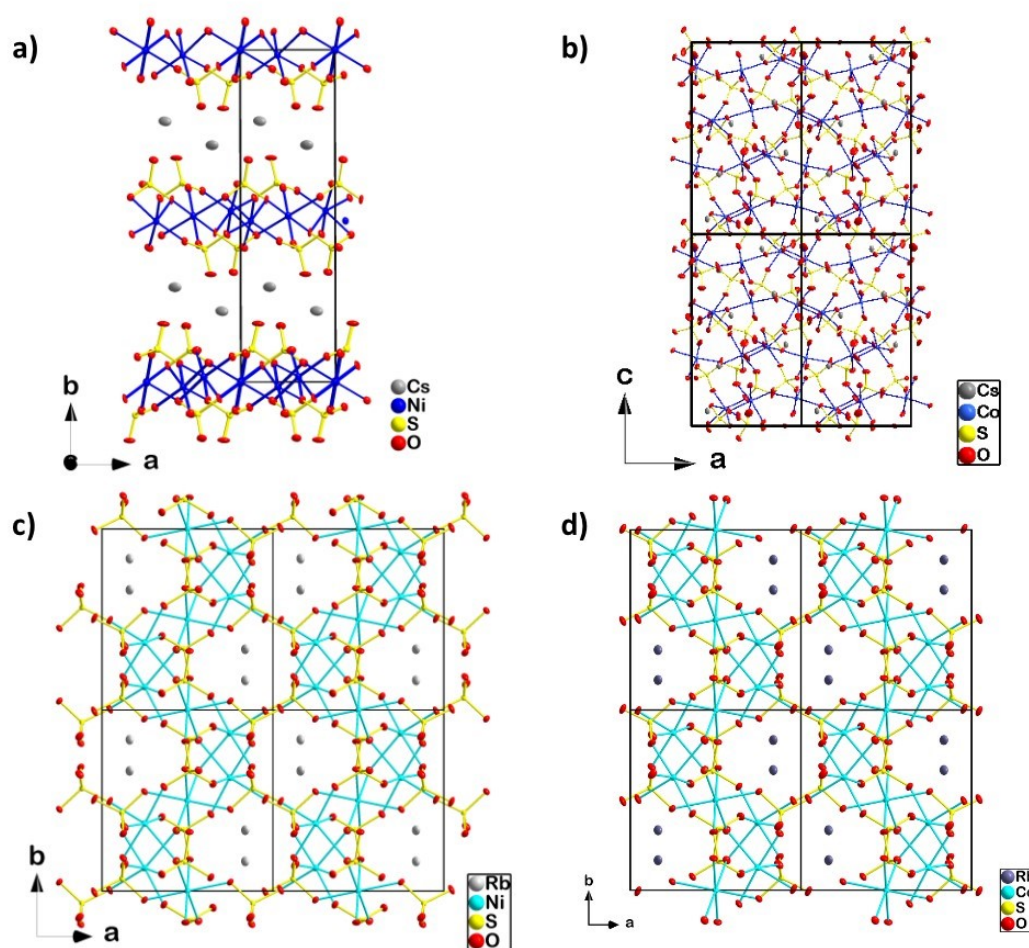


Figure S1. Crystal structure of a) $Cs_2Ni_3(SO_4)_4$, $Cs_2Co_3(SO_4)_4$, $Rb_2Ni_3(SO_4)_4$ and $Rb_2Co_3(SO_4)_4$ with ADPs. M-O bonds are drawn in blue and S-O bonds in yellow.

Table S1. Atomic coordinates and equivalent isotropic and anisotropic displacement parameters for **1** $Cs_2Ni_3(SO_4)_4$

Wyckoff site	x	y	z	U(eq)	U11	U22	U33	U23	U13	U12	
Cs(1)	2a	0.20139(13)	0.78636(3)	0.35957(8)	0.0362(2)	0.0498(4)	0.0302(3)	0.0374(4)	-0.0015(3)	0.0275(3)	-0.0061(2)
Ni(1)	2a	0	1	0	0.0137(4)	0.0124(7)	0.0197(7)	0.0086(7)	0.0001(5)	0.0018(5)	-0.0002(5)
Ni(2)	2a	-0.10736(18)	0.51544(5)	0.17902(12)	0.0124(3)	0.0111(5)	0.0178(5)	0.0078(5)	0.0002(4)	0.0012(4)	0.0001(3)
S(1)	2a	0.0386(4)	0.59580(9)	0.5735(2)	0.0129(6)	0.0127(10)	0.0155(9)	0.0101(9)	-0.0002(7)	0.0024(7)	0.0002(6)
S(2)	2a	-0.1194(4)	0.90037(9)	0.6318(2)	0.0122(6)	0.0113(10)	0.0145(9)	0.0097(9)	-0.0005(7)	0.0005(7)	-0.0010(6)
O(1)	2a	0.0914(10)	0.9239(3)	0.5506(7)	0.0153(18)	0.012(3)	0.022(3)	0.011(3)	0.000(2)	0.001(2)	0.000(2)
O(2)	2a	-0.1827(11)	0.8245(3)	0.5931(7)	0.024(2)	0.042(4)	0.010(3)	0.022(3)	0.000(2)	0.012(3)	-0.001(2)
O(3)	2a	0.0819(11)	0.6691(3)	0.6413(7)	0.0190(18)	0.024(3)	0.017(3)	0.016(3)	-0.001(2)	0.005(2)	-0.005(2)
O(4)	2a	0.2715(9)	0.5492(3)	0.6487(7)	0.0149(18)	0.005(3)	0.027(3)	0.011(3)	0.004(2)	-0.001(2)	0.004(2)
O(5)	2a	0.3381(10)	0.9426(3)	0.1493(6)	0.0148(17)	0.016(3)	0.020(3)	0.008(2)	-0.001(2)	0.002(2)	-0.0014(19)
O(6)	2a	-0.3525(9)	0.9454(3)	0.5413(7)	0.0141(18)	0.010(3)	0.021(3)	0.010(3)	0.004(2)	0.000(2)	0.0035(19)
O(7)	2a	-0.0300(10)	0.5950(3)	0.3770(6)	0.0171(18)	0.023(3)	0.021(3)	0.007(3)	-0.004(2)	0.003(2)	-0.001(2)
O(8)	2a	-0.0546(10)	0.9151(3)	0.8281(7)	0.0181(18)	0.014(3)	0.026(3)	0.012(3)	0.001(2)	-0.001(2)	-0.001(2)

Table S2. Atomic coordinates and equivalent isotropic and anisotropic displacement parameters for **2** $\text{Cs}_2\text{Co}_3(\text{SO}_4)_4$

	Wyck off	x	y	z	U(eq)	U11	U22	U33	U23	U13	U12
Cs(1)	4a	-0.14105(4)	0.47657(3)	0.42298(2)	0.02193(9)	0.01622(14)	0.01649(13)	0.03309(18)	-0.00032(12)	0.00034(14)	0.00060(10)
Cs(2)	4a	0.25018(4)	0.71357(3)	0.81336(2)	0.02164(9)	0.02081(15)	0.01476(13)	0.02934(17)	0.00212(13)	0.00029(15)	-0.00107(10)
Co(1)	4a	0.95950(7)	0.84028(6)	0.63115(4)	0.01143(17)	0.0108(3)	0.0110(3)	0.0125(3)	0.0015(2)	0.0013(2)	0.0008(2)
Co(2)	4a	0.54592(7)	0.56834(6)	0.64524(4)	0.01240(17)	0.0120(3)	0.0118(3)	0.0134(3)	-0.0027(2)	-0.0018(2)	-0.0007(2)
Co(3)	4a	0.19322(7)	0.40301(6)	0.59038(4)	0.01227(17)	0.0117(3)	0.0111(3)	0.0140(3)	-0.0016(2)	0.0005(2)	-0.0022(2)
S(1)	4a	-0.08849(12)	0.53524(11)	0.70152(7)	0.0100(3)	0.0080(4)	0.0093(4)	0.0127(5)	0.0002(4)	0.0009(4)	-0.0002(4)
S(2)	4a	0.24371(14)	0.66934(10)	0.53825(7)	0.0104(3)	0.0087(5)	0.0087(4)	0.0138(5)	0.0008(4)	0.0008(4)	-0.0003(4)
S(3)	4a	0.63757(13)	0.85710(10)	0.73474(7)	0.0098(3)	0.0100(5)	0.0085(4)	0.0108(5)	0.0004(4)	0.0006(4)	-0.0014(3)
S(4)	4a	0.49385(13)	0.37045(11)	0.48940(7)	0.0103(3)	0.0094(5)	0.0090(4)	0.0124(5)	0.0018(4)	0.0005(4)	-0.0019(4)
O(1)	4a	0.6918(4)	0.8012(4)	0.8145(2)	0.0189(10)	0.0276(19)	0.0168(16)	0.0124(15)	0.0044(14)	-0.0035(15)	0.0025(13)
O(2)	4a	0.5391(4)	0.9740(3)	0.7497(2)	0.0163(9)	0.0182(17)	0.0146(14)	0.0161(15)	0.0066(14)	0.0004(14)	-0.0027(13)
O(3)	4a	0.1492(4)	0.5668(3)	0.4992(2)	0.0174(9)	0.0160(17)	0.0165(15)	0.0198(16)	-0.0057(14)	-0.0038(14)	0.0011(13)
O(4)	4a	0.1595(4)	0.7774(4)	0.5779(3)	0.0241(10)	0.0151(17)	0.0171(16)	0.040(2)	0.0053(14)	0.0099(17)	-0.0053(13)
O(5)	4a	-0.0327(4)	0.6737(3)	0.7111(2)	0.0208(10)	0.027(2)	0.0103(14)	0.0252(18)	-0.0050(14)	-0.0056(16)	0.0023(13)
O(6)	4a	0.5463(4)	0.7559(4)	0.6907(3)	0.0222(10)	0.0195(18)	0.0162(16)	0.031(2)	-0.0020(14)	-0.0069(17)	-0.0077(13)
O(7)	4a	0.3459(4)	0.3214(4)	0.5110(2)	0.0229(11)	0.0197(19)	0.0246(18)	0.0244(19)	-0.0073(16)	0.0100(16)	-0.0057(13)
O(8)	4a	0.7593(4)	0.9032(3)	0.6816(2)	0.0195(9)	0.0154(16)	0.0204(16)	0.0228(17)	0.0037(15)	0.0075(16)	0.0055(13)
O(9)	4a	0.3473(4)	0.7316(4)	0.4795(2)	0.0212(10)	0.0221(19)	0.0187(17)	0.0229(18)	-0.0085(15)	0.0104(16)	-0.0037(13)
O(10)	4a	0.3250(4)	0.5928(3)	0.6061(2)	0.0183(10)	0.0170(18)	0.0167(16)	0.0212(17)	-0.0003(13)	-0.0073(14)	0.0042(13)
O(11)	4a	0.0021(5)	0.4601(4)	0.6425(3)	0.0390(16)	0.039(3)	0.029(2)	0.049(3)	0.007(2)	0.028(2)	-0.007(2)
O(12)	4a	-0.2370(5)	0.5393(4)	0.6678(3)	0.0387(14)	0.017(2)	0.030(2)	0.069(3)	-0.0045(19)	-0.019(2)	0.005(2)
O(13)	4a	-0.0914(5)	0.4637(4)	0.7817(2)	0.0290(13)	0.048(3)	0.0201(18)	0.0190(18)	0.0013(18)	-0.0017(18)	0.0061(13)
O(14)	4a	0.5748(5)	0.2623(4)	0.4496(3)	0.0387(14)	0.021(2)	0.031(2)	0.064(3)	0.0133(18)	-0.005(2)	-0.031(2)
O(15)	4a	0.4799(6)	0.4820(5)	0.4322(3)	0.0473(17)	0.052(3)	0.039(3)	0.051(3)	-0.002(2)	0.009(3)	0.033(2)
O(16)	4a	0.5736(5)	0.4153(5)	0.5649(3)	0.0353(14)	0.023(2)	0.050(3)	0.033(2)	0.011(2)	-0.0116(18)	-0.027(2)

Table S3. Atomic coordinates and equivalent isotropic and anisotropic displacement parameters for **3**
 $\text{Rb}_2\text{Ni}_3(\text{SO}_4)_4$

	Wyckoff site	x	y	z	U(eq)	U11	U22	U33	U23	U13	U12
Rb(1)	4e	0.16190(3)	0.83602(3)	0.10182(4)	0.02202(11)	0.01613(13)	0.02297(15)	0.03236(16)	-0.00033(11)	0.01601(12)	-0.00377(12)
Ni(1)	2b		0.5	1	0	0.00840(16)	0.0092(2)	0.0079(2)	0.0089(2)	0.00033(16)	0.00503(16)
Ni(2)	4e	-0.25109(4)	0.62716(4)	0.01507(4)	0.00943(11)	0.00919(14)	0.01071(15)	0.00957(15)	-0.00217(11)	0.00548(12)	-0.00246(11)
S(1)	4e	0.51722(7)	0.66243(7)	0.18910(7)	0.00719(18)	0.0078(2)	0.0078(3)	0.0069(2)	-0.0008(2)	0.0043(2)	-0.00008(19)
S(2)	4e	-0.11674(7)	0.93268(7)	0.24675(7)	0.0077(2)	0.0072(2)	0.0081(3)	0.0083(3)	-0.00051(19)	0.0042(2)	-0.00063(19)
O(1)	4e	-0.1245(2)	0.8167(2)	0.1261(2)	0.0129(6)	0.0131(8)	0.0130(9)	0.0138(8)	-0.0030(7)	0.0075(7)	-0.0063(7)
O(2)	4e	0.4884(2)	0.8260(2)	0.1352(2)	0.0126(7)	0.0169(9)	0.0089(8)	0.0141(8)	-0.0001(7)	0.0092(7)	0.0036(7)
O(3)	4e	0.3630(2)	0.5754(2)	0.0980(2)	0.0142(7)	0.0115(8)	0.0150(9)	0.0158(9)	-0.0041(7)	0.0063(7)	-0.0056(7)
O(4)	4e	0.0446(2)	1.0073(2)	0.3085(2)	0.0172(7)	0.0106(8)	0.0227(10)	0.0179(9)	-0.0081(8)	0.0065(7)	-0.0079(8)
O(5)	4e	0.3501(2)	1.0920(2)	0.3318(2)	0.0133(7)	0.0127(8)	0.0151(9)	0.0169(9)	-0.0017(7)	0.0109(7)	-0.0002(7)
O(6)	4e	0.5648(2)	0.8337(2)	-0.1322(2)	0.0114(6)	0.0133(8)	0.0141(8)	0.0064(8)	0.0009(7)	0.0045(7)	-0.0013(6)
O(7)	4e	0.2491(2)	0.9508(2)	-0.1617(2)	0.0118(6)	0.0106(8)	0.0117(8)	0.0122(8)	0.0034(7)	0.0048(7)	0.0028(7)
O(8)	4e	0.1314(2)	0.3552(2)	0.1202(2)	0.0145(7)	0.0171(9)	0.0181(10)	0.0125(9)	-0.0053(7)	0.0104(7)	-0.0067(7)

Table S4. Atomic coordinates and equivalent isotropic and anisotropic displacement parameters for 4 $\text{Rb}_2\text{Co}_3(\text{SO}_4)_4$

Wyckoff site	x	y	z	U(eq)	U11	U22	U33	U23	U13	U12		
Rb(1)	4e	1.16213(2)	1.16676(2)	0.10348(3)	0.02433(8)	0.01793(8)	0.02490(10)	0.03623(13)	0.00042(7)	0.01794(8)	0.00442(8)	
Co(1)	2b		0.5	1	0	0.00917(10)	0.01051(12)	0.00837(12)	0.00960(14)	-0.00064(10)	0.00566(10)	-0.00144(11)
Co(2)	4e	0.74777(3)	1.37387(3)	0.01363(3)	0.01015(7)	0.00994(8)	0.01073(9)	0.01090(10)	0.00204(7)	0.00595(7)	0.00275(8)	
S(1)	4e	0.48255(5)	0.83820(4)	0.31066(5)	0.00783(11)	0.00831(13)	0.00830(14)	0.00773(16)	-0.00050(11)	0.00457(12)	-0.00006(13)	
S(2)	4e	0.88458(4)	1.06796(5)	0.24608(5)	0.00828(11)	0.00774(13)	0.00926(14)	0.00801(16)	0.00040(11)	0.00396(12)	0.00087(13)	
O(1)	4e	0.35219(16)	0.90911(15)	0.33221(17)	0.0152(4)	0.0153(5)	0.0167(6)	0.0192(6)	0.0023(4)	0.0129(5)	0.0003(5)	
O(2)	4e	0.36382(15)	0.42461(15)	0.10045(17)	0.0153(4)	0.0125(5)	0.0153(5)	0.0181(6)	0.0054(4)	0.0075(5)	0.0064(5)	
O(3)	4e	0.95590(16)	1.49412(17)	0.19357(18)	0.0192(5)	0.0120(5)	0.0240(6)	0.0205(7)	-0.0080(5)	0.0070(5)	-0.0085(6)	
O(4)	4e	0.87512(16)	1.18443(15)	0.12703(17)	0.0149(4)	0.0162(5)	0.0145(5)	0.0167(6)	0.0043(4)	0.0102(5)	0.0080(5)	
O(5)	4e	0.51180(16)	0.67705(14)	0.36682(17)	0.0149(4)	0.0188(5)	0.0101(5)	0.0174(6)	0.0013(4)	0.0100(5)	0.0051(5)	
O(6)	4e	0.87062(17)	1.14308(16)	0.37886(17)	0.0172(5)	0.0204(6)	0.0201(6)	0.0159(6)	-0.0070(5)	0.0127(5)	-0.0078(5)	
O(7)	4e	0.75352(15)	0.95266(15)	0.16169(16)	0.0136(4)	0.0123(5)	0.0124(5)	0.0149(6)	-0.0031(4)	0.0058(4)	-0.0025(5)	
O(8)	4e	0.43494(15)	0.83290(15)	0.13422(15)	0.0138(4)	0.0160(5)	0.0176(6)	0.0081(5)	-0.0024(4)	0.0062(4)	0.0000(5)	

Table S5. Bond Valence Sums for 1 $\text{Cs}_2\text{Ni}_3(\text{SO}_4)_4$, 2 $\text{Cs}_2\text{Co}_3(\text{SO}_4)_4$, 3 $\text{Rb}_2\text{Ni}_3(\text{SO}_4)_4$ and 4 $\text{Rb}_2\text{Co}_3(\text{SO}_4)_4$ calculated using ref*.

1 $\text{Cs}_2\text{Ni}_3(\text{SO}_4)_4$		2 $\text{Cs}_2\text{Co}_3(\text{SO}_4)_4$				3 $\text{Rb}_2\text{Ni}_3(\text{SO}_4)_4$		4 $\text{Rb}_2\text{Co}_3(\text{SO}_4)_4$	
atoms	BVS	atoms	BVS	atoms	BVS	atoms	BVS	atoms	BVS
Cs1	1.050(6)	Cs1	1.204(4)	O5	2.034(14)	Rb1	1.291(3)	Rb1	1.1517(18)
Ni1	1.915(12)	Cs2	1.212(4)	O6	2.052(18)	Ni1	1.926(4)	Co1	1.957(3)
Ni2	1.915(12)	Co1	1.973(9)	O7	2.166(16)	Ni2	1.915(4)	Co2	1.964(3)
S1	5.97(4)	Co2	1.984(10)	O8	2.071(16)	S1	6.014(16)	S1	6.031(12)
S2	5.92(5)	Co3	2.007(9)	O9	1.946(16)	S2	6.062(16)	S2	6.083(13)
O1	2.01(3)	S1	6.29(3)	O10	1.959(13)	O1	2.202(9)	O1	2.010(8)
O2	2.02(3)	S2	6.02(3)	O11	2.13(2)	O2	2.113(8)	O2	2.077(5)
O3	2.01(3)	S3	6.04(3)	O12	2.13(2)	O3	2.071(8)	O3	1.990(6)
O4	1.97(2)	S4	6.34(4)	O13	2.013(15)	O4	2.014(8)	O4	2.170(7)
O5	1.89(2)	O1	1.967(15)	O14	2.14(2)	O5	2.027(10)	O5	2.119(6)
O6	2.01(2)	O2	2.090(14)	O15	2.18(2)	O6	1.816(8)	O6	2.016(8)
O7	1.98(2)	O3	1.967(14)	O16	2.14(2)	O7	1.978(7)	O7	1.976(5)
O8	1.91(2)	O4	2.091(18)			O8	2.024(9)	O8	1.850(6)

*Gagne and Hawthorne, Acta Cryst. 2015, B71, 562-578.

Table S6. Bond lengths (in Å) for $A_2M_3(\text{SO}_4)_4$ ($A = \text{Rb}, \text{Cs}$ $M = \text{Co}, \text{Ni}$)

(1) $\text{Cs}_2\text{Ni}_3(\text{SO}_4)_4$		(2) $\text{Cs}_2\text{Co}_3(\text{SO}_4)_4$				(3) $\text{Rb}_2\text{Ni}_3(\text{SO}_4)_4$		(4) $\text{Rb}_2\text{Co}_3(\text{SO}_4)_4$	
Cs(1)-O(1)	3.043(5) x2	Cs(1)-O(3)	3.027(4)	Co(2)-O(6)	1.995(3)	Rb(1)-O(1)	2.7751(18)	Rb(1)-O(4)	2.8072(13)
Cs(1)-O(3)	3.058(5)	Cs(1)-O(4)	3.036(4)	Co(2)-O(16)	2.003(4)	Rb(1)-O(2)	2.8889(19)	Rb(1)-O(2)	2.9297(13)
Cs(1)-O(2)	3.128(6)	Cs(1)-O(7)	3.137(4)	Co(2)-O(12)	2.021(4)	Rb(1)-O(3)	2.9201(19)	Rb(1)-O(5)	2.9304(14)
Cs(1)-O(3)	3.212(5)	Cs(1)-O(2)	3.227(3)	Co(2)-O(2)	2.060(3)	Rb(1)-O(5)	2.9672(18)	Rb(1)-O(6)	2.9973(14)

Cs(1)-O(2)	3.424(6)	Cs(1)-O(1)	3.279(3)	Co(2)-O(10)	2.109(3)	Rb(1)-O(8)	2.9811(18)	Rb(1)-O(1)	3.0003(14)
Cs(1)-O(3)	3.437(6)	Cs(1)-O(9)	3.284(3)			Rb(1)-O(4)	3.0073(19)	Rb(1)-O(3)	3.0194(15)
Cs(1)-O(5)	3.449(5)	Cs(1)-O(13)	3.354(4)	Co(3)-O(11)	1.999(4)	Rb(1)-O(7)	3.0871(18)	Rb(1)-O(7)	3.1278(14)
		Cs(1)-O(14)	3.366(5)	Co(3)-O(7)	2.038(4)	Rb(1)-O(7)	3.1300(18)	Rb(1)-O(7)	3.1426(14)
Ni(1)-O(8)	2.006(5)	Cs(1)-O(15)	3.434(6)	Co(3)-O(14)	2.061(4)				
Ni(1)-O(8)	2.006(5)	Cs(1)-O(16)	3.482(5)	Co(3)-O(1)	2.090(4)	Ni(1)-O(2)	1.9856(17)	Co(1)-O(5)	2.0112(13)
Ni(1)-O(4)	2.077(5)x2			Co(3)-O(3)	2.209(3)	Ni(1)-O(2)	1.9856(17)	Co(1)-O(5)	2.0112(13)
Ni(1)-O(5)	2.165(5)x2	Cs(2)-O(5)	3.058(4)	Co(3)-O(10)	2.240(3)	Ni(1)-O(7)	2.1097(17)	Co(1)-O(7)	2.1438(13)
		Cs(2)-O(8)	3.080(3)			Ni(1)-O(7)	2.1097(17)	Co(1)-O(7)	2.1438(13)
Ni(2)-O(1)	2.009(5)	Cs(2)-O(16)	3.201(4)	S(1)-O(12)	1.447(4)	Ni(1)-O(6)	2.1481(17)	Co(1)-O(8)	2.1874(13)
Ni(2)-O(6)	2.056(5)	Cs(2)-O(2)	3.207(4)	S(1)-O(11)	1.453(4)	Ni(1)-O(6)	2.1481(17)	Co(1)-O(8)	2.1874(13)
Ni(2)-O(7)	2.061(5)	Cs(2)-O(13)	3.241(4)	S(1)-O(13)	1.456(4)				
Ni(2)-O(6)	2.077(5)	Cs(2)-O(12)	3.243(4)	S(1)-O(5)	1.472(3)	Ni(2)-O(1)	1.9759(17)	Co(2)-O(4)	1.9990(13)
Ni(2)-O(4)	2.118(5)	Cs(2)-O(7)	3.270(4)			Ni(2)-O(3)	2.0332(18)	Co(2)-O(2)	2.0439(13)
Ni(2)-O(5)	2.155(5)	Cs(2)-O(6)	3.338(4)	S(2)-O(9)	1.459(4)	Ni(2)-O(8)	2.0457(18)	Co(2)-O(6)	2.0885(14)
		Cs(2)-O(15)	3.411(6)	S(2)-O(4)	1.461(3)	Ni(2)-O(5)	2.0537(17)	Co(2)-O(1)	2.0922(13)
S(1)-O(3)	1.438(5)	Cs(2)-O(11)	3.416(4)	S(2)-O(3)	1.470(4)	Ni(2)-O(4)	2.0880(17)	Co(2)-O(3)	2.1265(13)
S(1)-O(7)	1.445(5)			S(2)-O(10)	1.511(3)	Ni(2)-O(6)	2.3770(17)	Co(2)-O(8)	2.3938(13)
S(1)-O(4)	1.509(5)	Co(1)-O(15)	2.044(4)						
S(1)-O(5)	1.521(5)	Co(1)-O(8)	2.077(4)	S(3)-O(8)	1.463(4)	S(1)-O(3)	1.4639(18)	S(1)-O(1)	1.4658(13)
		Co(1)-O(5)	2.085(3)	S(3)-O(1)	1.469(3)	S(1)-O(5)	1.4649(18)	S(1)-O(5)	1.4663(13)
S(2)-O(2)	1.446(5)	Co(1)-O(4)	2.093(3)	S(3)-O(6)	1.477(4)	S(1)-O(2)	1.4688(18)	S(1)-O(2)	1.4678(13)
S(2)-O(8)	1.469(5)	Co(1)-O(9)	2.150(4)	S(3)-O(2)	1.482(3)	S(1)-O(6)	1.4967(17)	S(1)-O(8)	1.4896(14)
S(2)-O(1)	1.488(5)	Co(1)-O(13)	2.200(4)						
S(2)-O(6)	1.517(5)			S(4)-O(15)	1.431(4)	S(2)-O(4)	1.4634(18)	S(2)-O(3)	1.4614(13)
				S(4)-O(14)	1.442(4)	S(2)-O(8)	1.4654(18)	S(2)-O(6)	1.4651(14)
				S(4)-O(16)	1.467(4)	S(2)-O(1)	1.4734(18)	S(2)-O(4)	1.4728(13)
				S(4)-O(7)	1.468(4)	S(2)-O(7)	1.4784(18)	S(2)-O(7)	1.4766(13)