Supplementary data for:

The Relationship between the Crystal Structure and Electrical Properties of Oxide Ion Conducting $Ba_3W_{1.2}Nb_{0.8}O_{8.6}$

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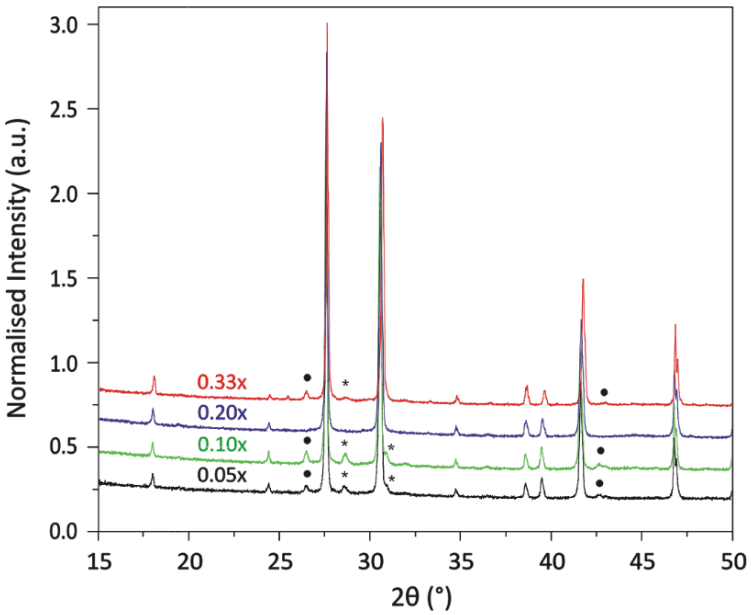

Figure S1. X-ray diffraction patterns of the $Ba_3W_{1+x}Nb_{1-x}O_{8.5+x/2}$ phases. The main peaks of the impurity phases $BaWO_4$ and $Ba_9Nb_6WO_{27}$ are marked by a circle and asterisk respectively.

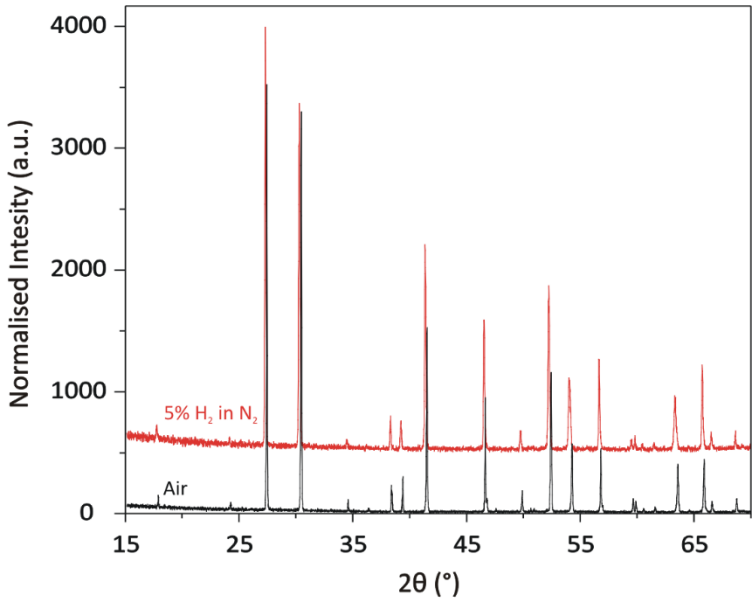

Figure S2. X-ray diffraction patterns of $Ba_3W_{1.2}Nb_{0.8}O_{8.6}$ as prepared (black line) and after 24 hours annealing in 5% H_2 in N_2 at 600 °C (red line).

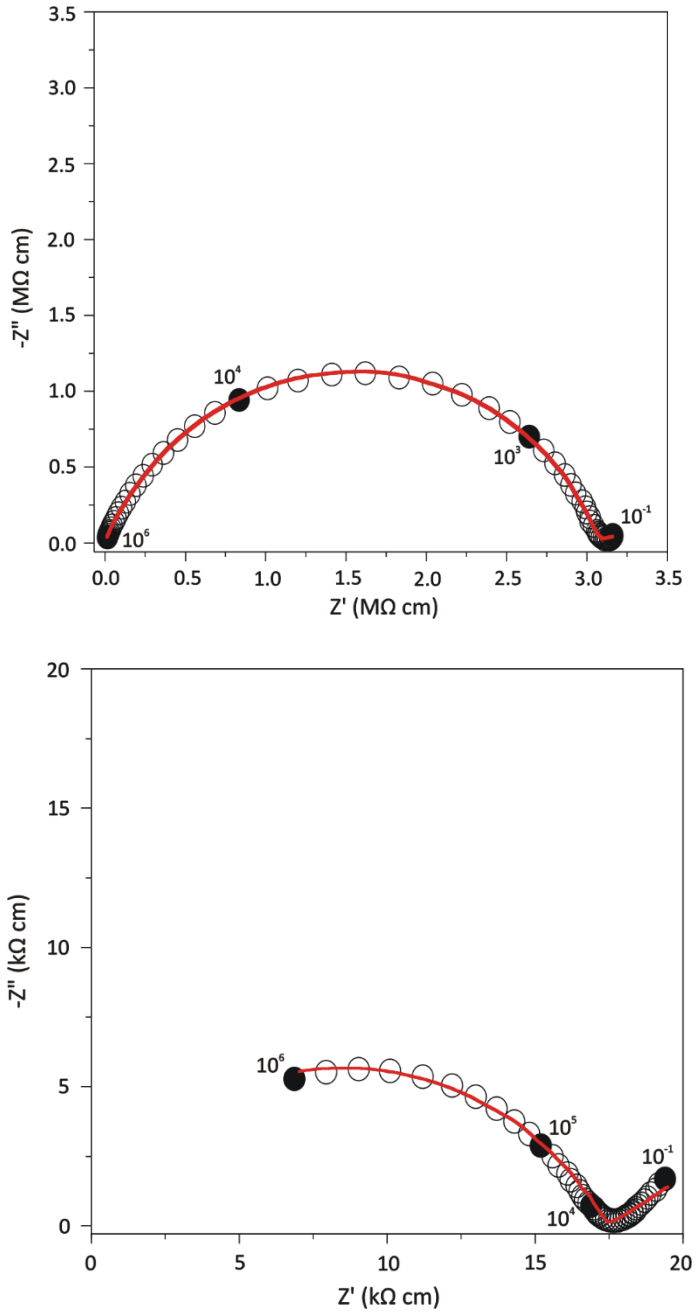

Figure S3 Complex impedance plots recorded in dry air at 400 °C (top) and 600 °C (bottom). An electrode response is observed in the low frequency region above 400 °C. The numbers and corresponding filled circles indicate selected frequencies (in Hz), while the red line is the equivalent circuit fitting.

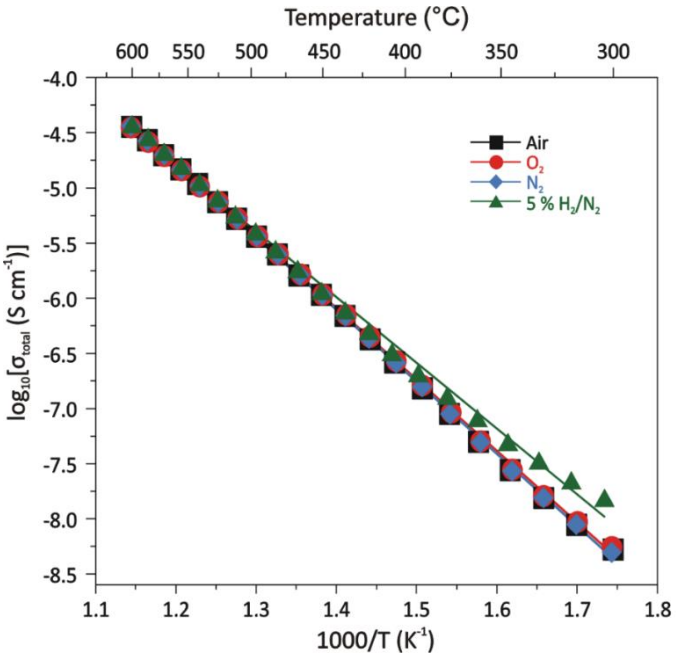

Figure S4. Arrhenius plot of the total conductivities of $Ba_3W_{1.2}Nb_{0.8}O_{8.6}$ recorded in a range of different atmospheres. Linear fits to the data are shown.

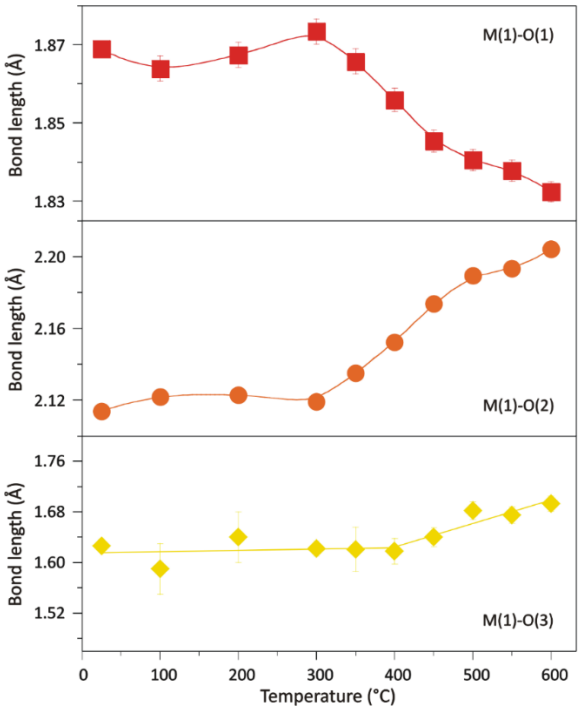

Figure S5. Temperature dependence of selected bond lengths for the M(1) polyhedra in $Ba_3W_{1.2}Nb_{0.8}O_{8.6}$.

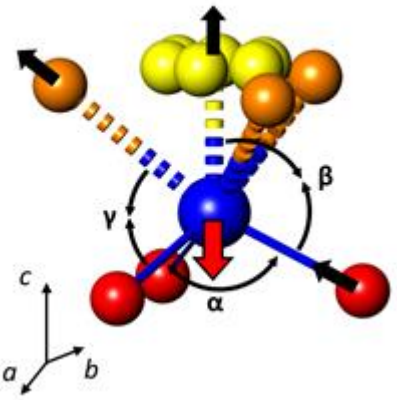

Figure S6. Representation of the M–O lattice relaxation; black arrows show the modifications of the bond lengths and angles at 600 °C from the "equilibrium" values at 25 °C.

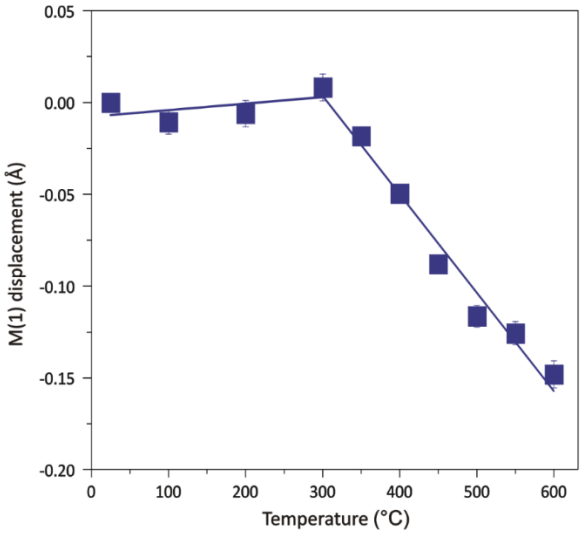

Figure S7. Variation of the displacement of the M(1) atom with temperature.

Table S1. Refined atomic parameters from the variable temperatures Rietveld fits. Neutron diffraction data of $Ba_3W_{1.2}Nb_{0.8}O_{8.6}$ were recorded on the D2B diffractometer (100-600 °C) and on the GEM diffractometer (25 °C). Data were refined in the space group $R\bar{3}m$ H. Atom positions are Ba(1) (0, 0, 0), Ba(2) (0, 0, z), M(1) (0, 0, z), M(2) (0, 0, ½) O(1) (x, y, z), O(2) (½, 0, 0), O(3) (x, y, z). U_{ij} indicates anisotropic thermal displacement parameters (in Å^2). U_{13} and U_{23} are zero due to the symmetry of the system. O(3) was refined with an isotropic thermal displacement parameter, U_{iso} (in Å^2).

Unit cell			**25 °C**	**100 °C**	**200 °C**	**300 °C**	**350 °C**	**400 °C**	**450 °C**	**500 °C**	**550 °C**	**600 °C**
***a* (Å)**			5.8431(1)	5.8512(2)	5.8582(2)	5.8672(1)	5.8794(1)	5.8975(2)	5.9134(2)	5.9251(2)	5.9338(1)	5.9421(1)
***c* (Å)**			21.0092(4)	21.0288(7)	21.0668(7)	21.1170(6)	21.1480(6)	21.1833(7)	21.2085(7)	21.2209(7)	21.2297(7)	21.2352(6)
V (Å^3)			621.20(3)	623.49(5)	626.12(5)	629.53(4)	633.09(4)	638.05(5)	642.27(5)	645.20(5)	647.34(4)	649.34(4)
Atom	**W**	**Parameter**	**25 °C**	**100 °C**	**200 °C**	**300 °C**	**350 °C**	**400 °C**	**450 °C**	**500 °C**	**550 °C**	**600 °C**
Ba(1)	**3*a***	**Occupancy**	1	1	1	1	1	1	1	1	1	1
		$U_{11} = U_{22}$ (Å^2)	0.011(1)	0.004(2)	0.009(2)	0.021(2)	0.026(3)	0.027(2)	0.037(3)	0.030(2)	0.033(2)	0.039(2)
		U_{33} (Å^2)	0.005(1)	0.023(3)	0.024(3)	0.019(3)	0.019(3)	0.016(3)	0.011(3)	0.012(3)	0.006(3)	-0.002(3)
		U_{12} (Å^2)	0.0056(5)	0.002(1)	0.004(1)	0.010(1)	0.013(1)	0.013(1)	0.019(1)	0.015(1)	0.016(1)	0.019(1)
Ba(2)	**6*c***	**z**	0.21060(8)	0.2101(2)	0.2104(2)	0.2105(2)	0.2104(2)	0.2098(2)	0.2089(3)	0.2082(3)	0.2082(3)	0.2078(3)
		Occupancy	1	1	1	1	1	1	1	1	1	1
		$U_{11} = U_{22}$ (Å^2)	0.0139(6)	0.014(1)	0.016(2)	0.020(1)	0.019(1)	0.027(2)	0.025(2)	0.032(2)	0.032(2)	0.034(2)
		U_{33} (Å^2)	0.0102(9)	0.017(2)	0.020(2)	0.020(2)	0.025(3)	0.030(3)	0.038(3)	0.046(3)	0.043(3)	0.043(3)
		U_{12} (Å^2)	0.0070(3)	0.0069(7)	0.0079(8)	0.0100(7)	0.0093(7)	0.0134(8)	0.0123(8)	0.0158(8)	0.0161(8)	0.0172(9)
M(1)	**6*c***	**z**	0.39397(9)	0.3944(2)	0.3943(2)	0.3937(2)	0.3946(2)	0.3955(2)	0.3968(2)	0.3977(2)	0.3979(2)	0.3985(2)
		Occupancy	0.910(2)	0.918(4)	0.921(4)	0.913(4)	0.913(4)	0.924(4)	0.934(4)	0.945(4)	0.949(4)	0.953(4)

		$U_{11} = U_{22}$ (Å^2)	0.0041(4)	0.005(1)	0.005(1)	0.0093(9)	0.010(1)	0.010(1)	0.011(1)	0.011(1)	0.012(1)	0.012(1)
		U_{33} (Å^2)	0.0422(9)	0.038(2)	0.043(2)	0.044(2)	0.043(2)	0.047(2)	0.044(3)	0.045(3)	0.051(3)	0.056(3)
		U_{12} (Å^2)	0.0020(2)	0.0024(5)	0.0027(5)	0.0047(5)	0.0048(5)	0.0051(5)	0.0057(5)	0.0056(5)	0.0062(5)	0.0058(5)
M(2)	**3*b***	**Occupancy**	0.181(2)	0.163(8)	0.159(8)	0.173(8)	0.175(8)	0.153(8)	0.131(8)	0.111(8)	0.103(8)	0.093(8)
		$U_{11} = U_{22}$ (Å^2)	0.0041(4)	0.005(1)	0.005(1)	0.0093(9)	0.010(1)	0.010(1)	0.011(1)	0.011(1)	0.012(1)	0.012(1)
		U_{33} (Å^2)	0.0422(9)	0.038(2)	0.043(2)	0.044(2)	0.043(2)	0.047(2)	0.044(3)	0.045(3)	0.051(3)	0.056(3)
		U_{12} (Å^2)	0.0020(2)	0.0024(5)	0.0027(5)	0.0047(5)	0.0048(5)	0.0051(5)	0.0057(5)	0.0056(5)	0.0062(5)	0.0058(5)
O(1)	**18*h***	**x**	0.17366(7)	0.1737(2)	0.1738(2)	0.1743(2)	0.1741(2)	0.1740(2)	0.1734(2)	0.1729(2)	0.1730(2)	0.1727(2)
		y	0.82634(7)	0.8263(2)	0.8262(2)	0.8257(2)	0.8259(2)	0.8260(2)	0.8266(2)	0.8271(2)	0.8270(2)	0.8273(2)
		z	0.10533(3)	0.10505(8)	0.10508(8)	0.10518(8)	0.10487(9)	0.10422(8)	0.10350(9)	0.10315(8)	0.10281(8)	0.10246(9)
		Occupancy	1	1	1	1	1	1	1	1	1	1
		U_{iso} (Å^2)	0.0145(1)	0.0166(5)	0.0194(5)	0.0229(4)	0.0250(5)	0.0288(5)	0.0311(6)	0.0331(6)	0.0352(6)	0.0373(6)
O(2)	**9*e***	**Occupancy**	0.791(2)	0.789(4)	0.795(5)	0.802(5)	0.769(5)	0.684(4)	0.632(2)	0.586(4)	0.567(4)	0.556(4)
		U_{iso} (Å^2)	0.0145(1)	0.0166(5)	0.0194(5)	0.0229(4)	0.0250(5)	0.0288(5)	0.0311(6)	0.0331(6)	0.0352(6)	0.0373(6)
O(3)	**18*h***	**x**	0.036(1)	0.030(4)	0.031(5)	0.037(5)	0.038(3)	0.039(2)	0.034(2)	0.039(1)	0.039(1)	0.041(1)
		y	0.072(3)	0.061(8)	0.063(9)	0.073(9)	0.076(7)	0.78(4)	0.068(3)	0.078(2)	0.078(2)	0.083(2)
		z	0.3185(7)	0.320(2)	0.318(2)	0.31890(8)	0.320(2)	0.3215(9)	0.3212(7)	0.3208(6)	0.3213(6)	0.3214(5)
		Occupancy	0.038(1)	0.039(2)	0.036(2)	0.033(2)	0.049(2)	0.091(2)	0.114(3)	0.140(2)	0.150(2)	0.155(2)
		U_{iso} (Å^2)	0.0145(1)	0.0166(5)	0.0194(5)	0.0229(4)	0.0250(5)	0.0288(5)	0.0311(6)	0.0331(6)	0.0352(6)	0.0373(6)
χ^2			4.035	2.659	2.518	2.320	2.273	2.485	2.755	2.780	2.843	2.739
R_p (%)			2.57	5.34	5.15	4.86	4.86	4.96	5.19	5.21	5.31	5.19
R_{wp} (%)			2.94	6.48	6.30	5.93	6.00	5.96	6.29	6.31	6.43	6.31

Table S2. Refined bond length values obtained from Rietveld fits at temperatures between 25 °C and 600 °C for $Ba_3W_{1.2}Nb_{0.8}O_{8.6}$.

Distance (Å)	25 °C	100 °C	200 °C	300 °C	350 °C	400 °C	450 °C	500 °C	550 °C	600 °C
Ba(1)-Ba(1)	5.8431(1)	5.8512(2)	5.8582(2)	5.8672(1)	5.8794(1)	5.8975(2)	5.9134(2)	5.9252(2)	5.9338(1)	5.9421(1)
Ba(1)-M(1)	3.6061(7)	3.6141(2)	3.618(2)	3.619(2)	3.633(2)	3.651(2)	3.670(2)	3.684(2)	3.690(2)	3.700(2)
Ba(1)-M(2)	4.86225(6)	4.8678(1)	4.8752(1)	4.88482(9)	4.8934(9)	4.9049(1)	4.9143(1)	4.9205(1)	4.9250(1)	4.92905(9)
Ba(1)-O(1)	2.8260(7)	2.824(2)	2.830(2)	2.841(2)	2.839(2)	2.834(2)	2.824(2)	2.818(2)	2.815(2)	2.810(2)
Ba(1)-O(2)	2.92156(5)	2.92559(9)	2.92911(9)	2.93358(7)	2.93970(7)	2.94873(8)	2.95671(8)	2.96257(8)	2.96688(7)	2.97107(7)
Ba(1)-O(3)	3.22182(5)	3.251(2)	3.25(2)	3.23(2)	3.23(1)	3.234(8)	3.263(7)	3.249(5)	3.253(5)	3.248(5)
Ba(2)-M(1)	3.6170(9)	3.623(3)	3.626(3)	3.636(3)	3.637(3)	3.645(3)	3.651(2)	3.656(3)	3.659(3)	3.662(2)
Ba(2)-M(1)	3.853(3)	3.877(6)	3.873(6)	3.868(6)	3.896(6)	3.934(6)	3.986(7)	4.023(7)	4.025(7)	4.050(7)
Ba(2)-M(2)	3.4975(4)	3.499(1)	3.506(1)	3.511(1)	3.518(1)	3.525(1)	3.529(1)	3.533(2)	3.538(1)	3.540(1)
Ba(2)-O(1)	2.825(2)	2.824(4)	2.834(4)	2.843(4)	2.849(4)	2.857(5)	2.854(5)	2.849(5)	2.858(5)	2.858(5)
Ba(2)-O(1)	2.9452(2)	2.9515(6)	2.9541(6)	2.9583(6)	2.9655(6)	2.9779(7)	2.9908(8)	2.9998(9)	3.0050(9)	3.0118(9)
Ba(2)-O(2)	3.081(1)	3.094(4)	3.093(4)	3.098(4)	3.106(4)	3.122(4)	3.144(4)	3.159(5)	3.160(5)	3.170(5)
Ba(2)-O(3)	2.2971(2)	2.34(4)	2.28(4)	2.320(9)	2.35(3)	2.40(2)	2.41(2)	2.42(1)	2.43(1)	2.45(1)
M(1)-M(2)	2.228(2)	2.221(5)	2.228(5)	2.246(5)	2.229(5)	2.214(5)	2.189(4)	2.170(4)	2.168(4)	2.155(4)
M(1)-O(1)	1.869(1)	1.864(3)	1.867(3)	1.873(3)	1.866(3)	1.856(3)	1.845(3)	1.841(3)	1.838(3)	1.832(3)
M(1)-O(2)	2.114(1)	2.122(3)	2.123(3)	2.119(3)	2.135(3)	2.152(3)	2.174(3)	2.189(3)	2.193(3)	2.204(3)
M(1)-O(3)	1.626(2)	1.59(4)	1.64(4)	1.62(1)	1.62(4)	1.62(2)	1.64(2)	1.68(1)	1.68(1)	1.69(1)
M(2)-O(1)	2.0668(7)	2.073(2)	2.075(2)	2.073(2)	2.083(2)	2.098(2)	2.116(2)	2.128(2)	2.134(2)	2.143(2)

O(2)-O(3)	1.35815(2)	1.41(4)	1.41(5)	1.36(5)	1.34(3)	1.33(2)	1.38(2)	1.34(1)	1.34(1)	1.31(1)
O(2)-O(3)	1.92086(3)	1.88(3)	1.90(3)	1.93(3)	1.94(2)	1.95(1)	1.92(1)	1.961(8)	1.963(8)	1.980(8)

Table S3. Refined bond angle values obtained from Rietveld fits at temperatures between 25 °C and 600 °C for $Ba_3W_{1.2}Nb_{0.8}O_{8.6}$.

Angle (°)	25 °C	100 °C	200 °C	300 °C	350 °C	400 °C	450 °C	500 °C	550 °C	600 °C
O(1)-M1-O(1)	96.97(8)	97.5(2)	97.3(2)	96.7(2)	97.7(2)	98.9(2)	100.5(2)	101.6(2)	101.9(2)	102.7(2)
O(1)-M1-O(2)	87.58(2)	87.41(5)	87.47(5)	87.66(5)	87.39(5)	86.95(5)	86.35(5)	85.95(6)	85.76(6)	85.43(6)
O(1)-M1-O(2)	173.1(1)	172.5(3)	172.7(3)	173.4(3)	172.3(3)	171.0(2)	169.2(2)	167.9(2)	167.6(2)	166.7(2)
O(1)-M1-O(3)	113.12(5)	113.8(9)	114(1)	113(1)	112.1(7)	110.9(4)	110.8(3)	109.1(3)	108.8(2)	107.7(2)
O(1)-M1-O(3)	133.12(7)	131(2)	131(2)	134(2)	133(1)	133.0(7)	129.7(6)	130.4(5)	130.2(5)	130.2(5)
O(2)-M1-O(2)	87.43(6)	87.2(2)	87.2(2)	87.6(2)	87.0(2)	86.5(1)	85.7(1)	85.2(1)	85.1(1)	84.7(1)
O(1)-M2-O(1)	85.24(3)	85.07(8)	85.04(8)	84.93(8)	84.80(8)	84.46(8)	84.20(8)	84.16(8)	83.96(8)	83.83(8)
O(1)-M2-O(1)	94.76(3)	94.93(8)	94.96(8)	95.07(8)	95.20(8)	95.54(8)	95.80(8)	95.84(8)	96.04(8)	96.17(8)
O(1)-M2-O(1)	180(0)	180(0)	180(0)	180(0)	180(0)	180(0)	180(0)	180(0)	180(0)	180(0)