Table 1S: Bond Lengths, Bond Angles, Spin Contamination Expectation Value ‹S^2› and Energies for MO_3 and their isomers $OM(O_2)$, OMOO and $M(O_3)$; M = Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu.

Cluster Model	State	$R_{M-O(1)}$[a] Å	$R_{M-O(2)}$[a] Å	R_{O-O} Å	$\angle O_{(2)}MO_{(2)}$ deg	$\angle O_{(2)}O_{(1)}O_{(2)}$ deg	‹S^2›	$\Delta E_{tot}\times10^2$ Hartree B1LYP/ CCSD(T)
$OSc(O_2)$ C_s	^{2}**A"**	1.677	2.122	1.329	36.5	23.0	0.758	0.000
$OTi(O_2)$ C_s	^{1}**A'**	1.619	1.828	1.470	47.4	28.5	0.000	0.000
TiO_3 C_{3v}	^{1}**A_1**	1.734			105.9		0.000	7.081 (3.152)
VO_3 C_s	^{2}**A"**	1.783	1.592		113.7	56.1	0.772	**0.000**
$OV(O_2)$ C_s	^{2}**A'**	1.585	1.805	1.451	47.4	27.5	0.769	3.647 (4.788)
CrO_3 C_{3v}	^{1}**A_1**	1.574			115.6		0.000	0.000
$OCr(O_2)$ C_{2v}	^{5}**A_2**	1.905	1.925	1.316	40.0		6.879	1.521 (10.20)
	^{3}**B_1**	1.612	2.000	1.321	38.6		3.031	6.266 (5.968)
	^{3}**A_2**	1.851	1.793	1.406	46.2		2.022	14.615
MnO_3 D_{3h}	^{2}**A_1'**	1.577			120.0		1.004	0.000
$OMn(O_2)$ C_{2v}	^{6}**B_1**	1.694	2.012	1.324	38.4		9.209	2.095 (4.331)
	^{4}**A_2**	1.740	1.823	1.407	46.4		4.650	2.703 (5.131)
$Mn(O_3)$ C_{2v}	^{6}**A_1**		1.898	1.465	75.9	105.6	8.765	8.676 (6.942)
$OFe(O_2)$ C_{2v}	^{5}**B_2**	1.661	1.923	1.330	40.5		6.426	**0.000**
	^{3}**A_2**	1.723	1.823	1.386	44.7		3.011	1.791 (1.797)
FeO_3 D_{3h}	^{1}**A_1'**	1.555			120.0		0.000	1.882 (-4.696)
$OCo(O_2)$ C_{2v}	^{6}**A_1**	1.653	1.984	1.329	39.1		8.780	**0.000**
	^{4}**A_2**	1.659	1.984	1.329	39.1		4.742	0.429 (0.560)

	^{4}**B$_1$**	1.846	1.963	**1.321**	39.3		4.739	3.262
CoO_3 C_{2v}	^{2}**B$_1$**	1.623	1.555		128.0		0.781	5.446
	^{2}**B$_2$**	1.785	1.548		139.5		0.833	8.281
	^{2}**A$_1$**	1.750	1.618		152.5		1.846	10.548
$Co(O_3)$ C_{2v}	^{4}**A$_1$**		1.846	1.426	74.4	103.0	3.766	5.389
	^{2}**A$_1$**		2.128	1.342	62.7	111.1	1.733	7.816
	^{6}**A$_1$**		2.058	1.348	64.2	108.5	8.759	7.986
$ONi(O_2)$ C_{2v}	^{5}**A$_1$**	1.692	1.960	1.317	39.3		6.024	0.000
	^{3}**B$_1$**	1.688	1.892	1.350	41.8		2.487	2.288 (1.716)
$OCu(O_2)$ C_{2v}	^{4}**A$_1$**	1.755	1.978	1.290	38.1		3.777	0.000
	^{2}**A$_1$**	1.765	1.965	1.293	38.4		1.761	1.419 (1.474)
$Cu(O_3)$ C_{2v}	^{2}**B$_1$**		2.065	1.344	65.0	111.2	0.755	1.825
CuO_3 C_{2v}	^{6}**A$_1$**	1.827	1.872	1.958	63.1		8.809	11.281

oxo-super-oxides C_s	State	$R_{M-O(1)}$[a] Å	$R_{M-O(2)}$[a] Å	R_{O-O} Å	$\angle MO_{(2)}-O_{(3)}$ deg	$\angle OMO$ deg	$\langle S^2 \rangle$	$\Delta E_{tot}\times 10^2$ Hartree
OScOO	^{2}**A'**	1.674	1.963	1.306	162.3	125.4	0.755	2.919
OTiOO	^{3}**A'**	1.625	1.922	1.305	162.7	137.7	2.009	6.746 (7.813)
	^{1}**A'**	1.614	1.729	1.316	154.3	113.5	0.000	7.416 (7.074)
OVOO	^{4}**A'**	1.596	1.831	1.295	152.8	131.6	3.777	10.833
OCrOO	^{3}**A''**	1.572	1.789	1.291	157.8	140.2	2.943	10.840 (9.760)
	^{1}**A'**	1.575	1.690	1.289	158.9	149.3	0.000	14.984 (13.159)
OMnOO	^{6}**A'**	1.778	1.870	1.316	143.6	176.8	9.526	5.409 (7.921)
OFeOO	^{1}**A'**	1.582	1.667	1.253	142.3	121.9	0.000	12.599
OCoOO	^{6}**A'**	1.647	1.836	1.283	146.2	164.5	8.783	2.143
ONiOO	^{3}**A'**	1.749	1.790	1.245	147.7	155.4	2.909	3.054
ONiOO; $C_{\infty v}$	^{1}**Σ_g**	1.603	1.621	1.229	180.0	180.0	0.000	6.232

OCuOO	^{4}**A"**	1.767	1.863	1.231	132.8	178.3	3.772	0.506 (0.350)
	^{2}**A"**	1.775	1.878	1.220	137.4	180.0	1.754	0.725 (0.368)

[a] – in oxoperoxides OMO_2 and ozonides $M(O_3)$: (1) refers to oxygen atoms, positioned along the C_2 axis for cluster symmetry C_{2v} or in the σ plane for cluster symmetry C_s and (2) refers to the other two oxygen atoms in the σ_v plane of C_{2v} symmetry clusters or symmetrically displaced along the σ plane for C_s; in oxosuperoxides: O(1), O(2) and O(3) represent the non-equivalent oxygen atoms: O(1)-M-O(2)-O(3). R_{O-O} – interatomic distance between oxygen atoms in peroxides and superoxides. CCSD(T) values given in brackets.

ΔE_{tot} – total energy difference relative to the ground-state E_{tot} (Hartree):

ScO_3: -986.34053 by B1LYP; -985.04300 by CCSD(T)

TiO_3: -1075.09691 by B1LYP; -1073.76020 by CCSD(T)

VO_3: -1169.63842 by B1LYP; -1168.26094 by CCSD(T)

CrO_3: -1270.07446 by B1LYP; -1268.67241 by CCSD(T)

MnO_3: -1376.54899 by B1LYP; -1375.09403 by CCSD(T).

FeO_3: -1489.21968 by B1LYP; -1487.68841 by CCSD(T).

CoO_3: -1608.25820 by B1LYP; -1606.67961 by CCSD(T).

NiO_3: -1733.77203 by B1LYP; -1732.15805 by CCSD(T).

CuO_3: -1865.95311 by B1LYP; -1864.27845 by CCSD(T)

Table 2S: Bond Lengths, Bond Angles, Spin Contamination Expectation Value ‹S^2› and Energies for MO_3^-

Cluster Models	State	$R_{M-O(1)}$[a] Å	$R_{M-O(2)}$[a] Å	R_{O-O} Å	$\angle O_{(2)}MO_{(2)}$ deg	$\angle O_{(2)}O_{(1)}O_{(2)}$ deg	‹S^2›	$\Delta E_{tot}\times10^2$ Hartree B1LYP/ CCSD(T)
$OSc(O_2)^-$ C_s	**$^1A'$**	1.785	1.983	1.523	45.2	24.6	0.000	-7.376 (-7.373)
TiO_3^- C_{2v}	**$^2B_2$**	1.923	1.696		119.9		0.768	-13.475 (-12.290)
$OTi(O_2)^-$ C_s	**$^2A'$**	1.664	1.872	1.491	46.9	27.6	0.754	-6.067 (-5.450)
VO_3^- D_{3h}	**$^1A_1'$**	1.649			120.0		0.000	-15.479 (-15.022)
$OV(O_2)^-$ C_{2v}	**$^3A_2$**	1.667	1.898	1.523	47.3		2.023	-2.879 (-0.412)
	$^3B_2$	1.919	1.842	1.446	46.2		2.016	7.694 (-0.223)
CrO_3^- D_{3h}	**$^2A_1'$**	1.623			120.0		0.792	-14.696 (-12.776)
$OCr(O_2)^-$ C_{2v}	**$^4B_2$**	1.680	1.898	1.494	46.3		3.817	-2.267 (-2.06)
	$^6B_1$	1.688	2.124	1.328	36.4		8.827	-0.532 (-0.300)
	$^2B_1$	1.674	1.869	1.472	46.4		0.782	+2.702
MnO_3^- D_{3h}	**$^1A_1$'**	1.597			120.0		0.000	-13.176 (-13.005)
$OMn(O_2)^-$ C_{2v}	**$^5B_2$**	1.691	1.872	1.458	45.9		6.134	-8.369 (-1.409)
	$^3B_1$	1.666	1.940	1.354	40.8		2.744	-1.561 (+2.819)
	$^1A_1$	1.687	1.858	1.439	45.6		0.000	+4.950
FeO_3^- C_{2v}	**$^2B_1$**	1.615	1.593		125.2		0.778	-12.510
$OFe(O_2)^-$ C_{2v}	**$^4B_2$**	1.656	1.844	1.444	46.1		3.860	-10.192 (-9.906)
	$^2B_1$	1.668	1.993	1.322	38.7		1.912	-5.636 (-4.396)

	^{6}**B$_2$**	1.920	1.889	1.503	46.9		8.782	-5.285
CoO_3^- C_{2v}	^{5}**A$_1$**	1.653	1.699		91.1		6.047	-9.739 (-3.618)
$OCo(O_2)^-$ C_{2v}	^{3}**B$_2$**	1.665	1.827	1.415	45.6		2.131	-9.469 (-3.322)
	^{5}**A$_1$**	1.678	2.056	1.344	38.14		6.049	-8.941
	^{1}**A$_1$**	1.625	1.854	1.439	45.7		0.000	-2.434
$Co(O_3)^-$ C_{2v}	^{5}**A$_1$**	2.455	1.911	1.450	72.3	102.0	6.010	-1.157
	^{3}**B$_2$**	2.632	2.171	1.348	61.4	110.7	2.986	+2.951
$ONi(O_2)^-$	^{4}**A$_1$**	1.671	2.022	1.344	38.8		3.785	-10.273 (-10.724)
NiO_3^-	^{6}**B$_2$**	1.719	1.746		113.0		8.833	-8.206 (-7.839)
$OCu(O_2)^-$	^{1}**A$_1$**	1.692	1.860	1.393	44.0		0.000	-7.284

Oxo-superoxide	State	$R_{M-O(1)}$[a] Å	$R_{M-O(2)}$[a] Å	R_{O-O} Å	∠MOO deg	∠OMO deg	‹S^2›	$\Delta E_{tot}\times10^2$ Hartree
$OScOO^-$	^{3}**A'**	1.710	2.030	1.313	119.5	121.0	2.005	-2.240
	^{1}**A'**	1.760	1.870	1.401	159.6	142.5	0.000	-0.731
$OTiOO^-$	^{2}**A'**	1.648	1.743	1.366	155.1	116.5	0.778	-0.306 (+2.291)
	^{4}**A''**	1.663	2.038	1.326	132.2	135.2	3.763	+0.758 (+2.374)
$OVOO^-$	^{3}**A'**	1.641	1.850	1.324	155.9	136.9	2.739	+1.896 (+5.022)
	^{5}**A''**	1.649	1.962	1.311	161.4	158.3	6.038	+2.424 (5.285)
$OCrOO^-$	^{2}**A'**	1.630	1.700	1.350	163.4	152.2	0.790	+4.933 (+13.159)
$OMnOO^-$	^{3}**A''**	1.683	1.773	1.294	179.7	179.8	3.070	-2.117
	^{1}**A'**	1.615	1.646	1.327	159.9	139.2	0.000	+4.162
$OFeOO^-$	^{6}**A'**	1.670	1.957	1.334	126.0	174.1	8.778	-7.171
$OCoOO^-$	^{1}**Σ_g**	1.610	1.615	1.306	180.0	180.0	0.000	-3.940
$OCuOO^-$	^{3}**A'**	1.778	1.893	1.338	114.8	177.0	2.015	-10.081

[a] – notations as for Table 1S.