Supporting Information For

Studies of Oxalate Bridged MM Quadruple Bonds and Their Radical Cations (M = Mo or W): On the Matter of Linkage Isomers

Malcolm H. Chisholm*, *Jason S. D'Acchioli, Christopher M. Hadad*, and Nathan J. Patmore.*

[†]Department of Chemistry, The Ohio State University,

100 W. 18th Avenue, Columbus, OH 43210-1185 USA

Supporting Information

Figure S1. Representations of the 6 π orbitals of oxalate.

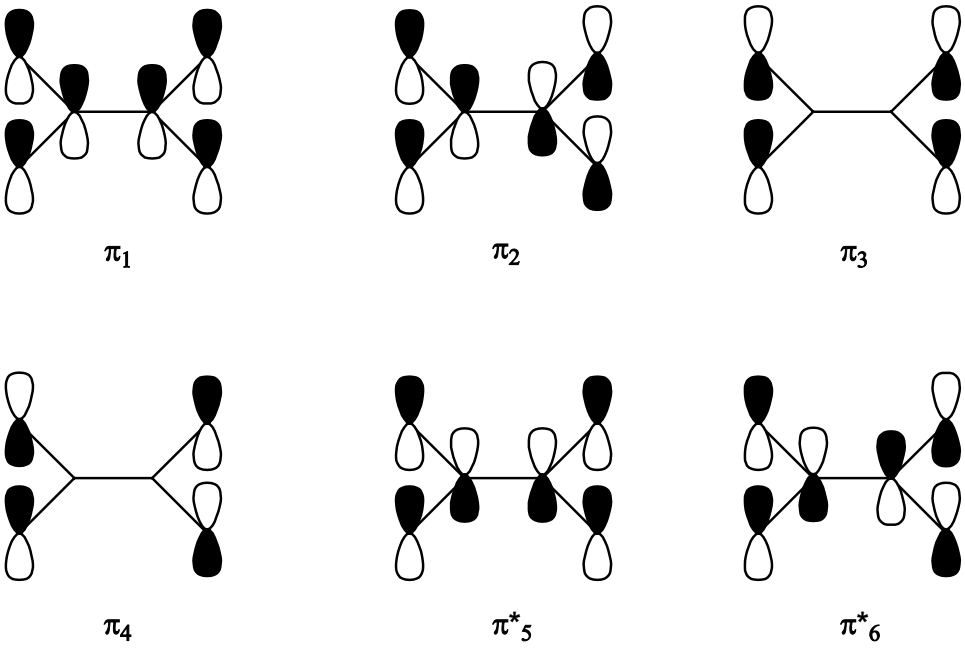


Table S1. Irreducible representations spanned by the 6 π orbitals of oxalate.

Oxalate π orbitals	Irreducible representations
π_1	b_{2u}
π_2	b_{3g}
π_3	b_{1g}
π_4	a_u
π_5*	b_{2u}
π_6*	b_{3g}

Figure S2. Electronic absorption spectra of $[Mo_2(O_2CBu^t)_3]_2(\mu\text{-}O_2CCO_2)^+PF_6^-$ in THF recorded at 10 minute intervals. The first spectrum (t = 5 minutes) is red, and the final spectrum (t = 95 minutes) is blue. The sharp feature in the spectra at around 2300 cm^{-1} is due to absorption from the sample cell glass.

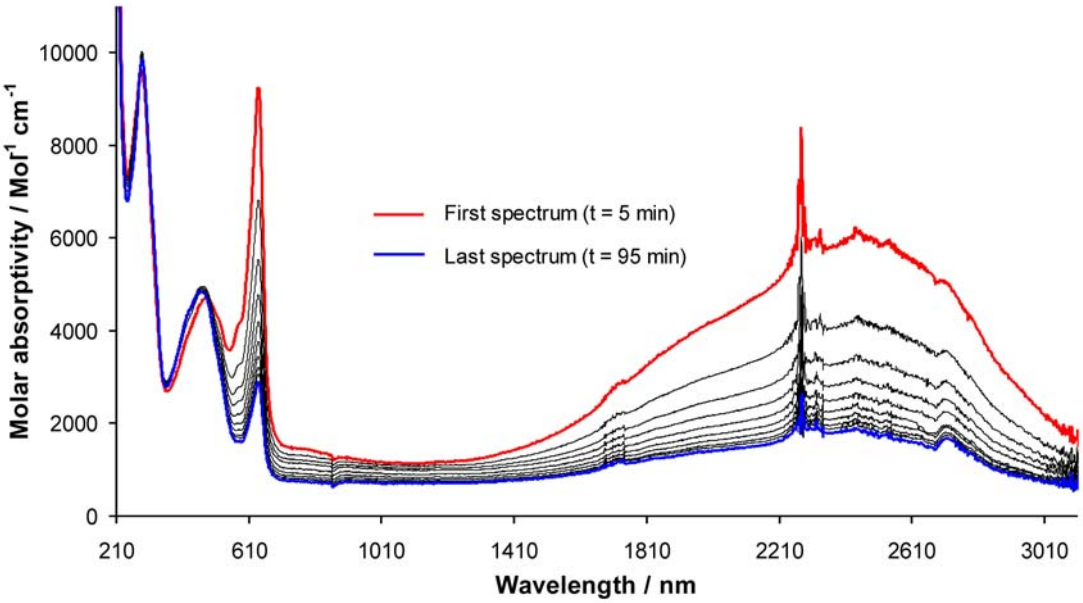
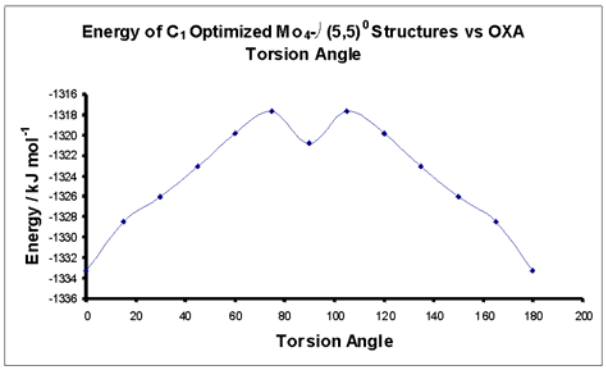
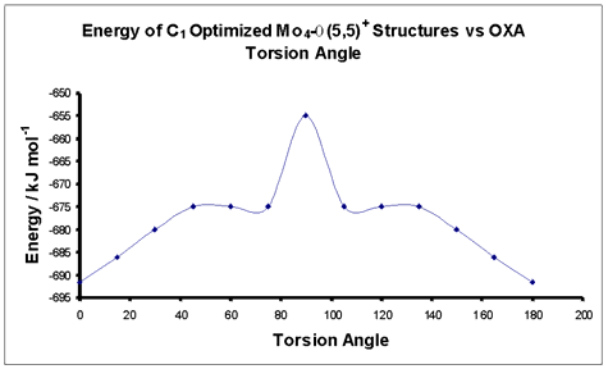


Figure S3. Relaxed potential energy surface scans for **a)** Mo_4-μ(5,5)^0; **b)** Mo_4-μ(5,5)$^+$; **c)** W_4-μ(5,5)^0; and **d)** Mo_4-μ(5,5)$^+$.

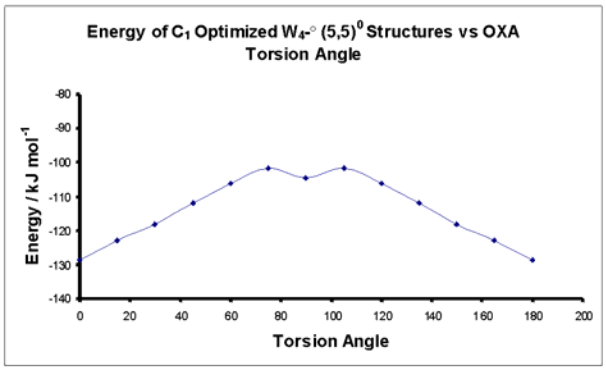
a.



b.



c.


Energy of C1 Optimized W4-◇ (5,5)0 Structures vs OXA Torsion Angle
Energy / kJ mol-1
-80
-90
-100
-110
-120
-130
-140
0
20
40
60
80
100
120
140
160
180
200
Torsion Angle

d.

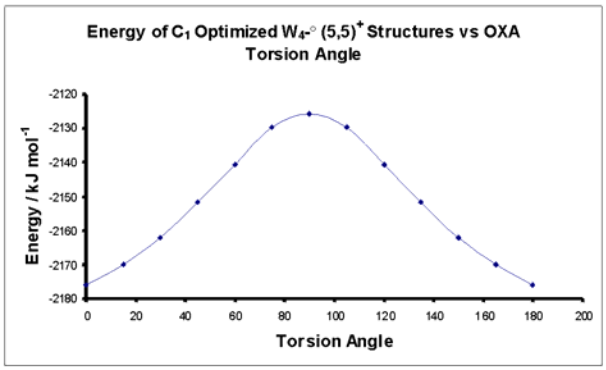

Energy of C1 Optimized W4-◇ (5,5)+ Structures vs OXA Torsion Angle
Energy / kJ mol-1
-2120
-2130
-2140
-2150
-2160
-2170
-2180
0
20
40
60
80
100
120
140
160
180
200
Torsion Angle

Table S2. Cartesian coordinates of $[Mo_2]_2$-μ(5,5)^0.

Atom	x	y	z
C	0.75160	0.00000	0.00000
C	-0.75160	0.00000	0.00000
O	-1.36505	0.00000	1.12005
O	-1.36505	0.00000	-1.12005
Mo	-3.46226	0.00000	1.06109
Mo	-3.46226	0.00000	-1.06109
O	-5.58468	0.00000	1.12167
O	-5.58468	0.00000	-1.12167
C	-6.18534	0.00000	0.00000
H	-7.27972	0.00000	0.00000
O	-3.47570	2.11984	1.12144
O	-3.47570	2.11984	-1.12144
C	-3.48198	2.72101	0.00000
H	-3.49271	3.81525	0.00000
O	-3.47570	-2.11984	-1.12144
O	-3.47570	-2.11984	1.12144
C	-3.48198	-2.72101	0.00000
H	-3.49271	-3.81525	0.00000
O	1.36505	0.00000	-1.12005
O	1.36505	0.00000	1.12005
Mo	3.46226	0.00000	-1.06109
Mo	3.46226	0.00000	1.06109
O	5.58468	0.00000	-1.12167
O	5.58468	0.00000	1.12167
C	6.18534	0.00000	0.00000
H	7.27972	0.00000	0.00000
O	3.47570	2.11984	-1.12144
O	3.47570	2.11984	1.12144
C	3.48198	2.72101	0.00000
H	3.49271	3.81525	0.00000
O	3.47570	-2.11984	1.12144
O	3.47570	-2.11984	-1.12144
C	3.48198	-2.72101	0.00000
H	3.49271	-3.81525	0.00000

Table S3. Cartesian coordinates of $[Mo_2]_2$-μ(5,5)$^+$.

Atom	x	y	z
C	0.74174	0.00000	0.00000
C	-0.74174	0.00000	0.00000
O	-1.36338	0.00000	1.12234
O	-1.36338	0.00000	-1.12234
Mo	-3.43442	0.00000	1.07392
Mo	-3.43442	0.00000	-1.07392
O	-5.53868	0.00000	1.12034
O	-5.53868	0.00000	-1.12034
C	-6.14577	0.00000	0.00000
H	-7.23858	0.00000	0.00000
O	-3.46460	2.10440	1.12061
O	-3.46460	2.10440	-1.12061
C	-3.48019	2.71073	0.00000
H	-3.50918	3.80327	0.00000
O	-3.46460	-2.10440	-1.12061
O	-3.46460	-2.10440	1.12061
C	-3.48019	-2.71073	0.00000
H	-3.50918	-3.80327	0.00000
O	1.36338	0.00000	-1.12234
O	1.36338	0.00000	1.12234
Mo	3.43442	0.00000	-1.07392
Mo	3.43442	0.00000	1.07392
O	5.53868	0.00000	-1.12034
O	5.53868	0.00000	1.12034
C	6.14577	0.00000	0.00000
H	7.23858	0.00000	0.00000
O	3.46460	2.10440	-1.12061
O	3.46460	2.10440	1.12061
C	3.48019	2.71073	0.00000
H	3.50918	3.80327	0.00000
O	3.46460	-2.10440	1.12061
O	3.46460	-2.10440	-1.12061
C	3.48019	-2.71073	0.00000
H	3.50918	-3.80327	0.00000

Table S4. Cartesian coordinates of $[Mo_2]_2$-μ(6,6)^0.

Atom	x	y	z
Mo	-3.168063	0.000000	1.060254
Mo	-3.168063	0.000000	-1.060254
O	-5.276533	0.000000	1.119493
O	-5.276533	0.000000	-1.119493
C	-5.882245	0.000000	0.000000
O	-3.165941	2.118953	1.121036
O	-3.165941	2.118953	-1.121036
C	-3.165243	2.720912	0.000000
O	-3.165941	-2.118953	-1.121036
O	-3.165941	-2.118953	1.121036
C	-3.165243	-2.720912	0.000000
Mo	3.168063	0.000000	1.060254
Mo	3.168063	0.000000	-1.060254
O	5.276533	0.000000	-1.119493
O	5.276533	0.000000	1.119493
C	5.882245	0.000000	0.000000
O	3.165941	2.118953	-1.121036
O	3.165941	2.118953	1.121036
C	3.165243	2.720912	0.000000
O	3.165941	-2.118953	1.121036
O	3.165941	-2.118953	-1.121036
C	3.165243	-2.720912	0.000000
H	-6.975863	0.000000	0.000000
H	-3.164011	3.815207	0.000000
H	-3.164011	-3.815207	0.000000
H	6.975863	0.000000	0.000000
H	3.164011	3.815207	0.000000
H	3.164011	-3.815207	0.000000
O	1.101340	0.000000	1.396783
C	0.000000	0.000000	0.765609
C	0.000000	0.000000	-0.765609
O	1.101340	0.000000	-1.396783
O	-1.101340	0.000000	-1.396783
O	-1.101340	0.000000	1.396783

Table S5. Cartesian coordinates of $[Mo_2]_2$-μ(6,6)$^+$.

Atom	x	y	z
Mo	-3.13259	0.00000	1.07365
Mo	-3.13259	0.00000	-1.07365
O	-5.22671	0.00000	1.11829
O	-5.22671	0.00000	-1.11829
C	-5.83741	0.00000	0.00000
O	-3.15848	2.10430	1.11977
O	-3.15848	2.10430	-1.11977
C	-3.17260	2.71155	0.00000
O	-3.15848	-2.10430	-1.11977
O	-3.15848	-2.10430	1.11977
C	-3.17260	-2.71155	0.00000
Mo	3.13259	0.00000	1.07365
Mo	3.13259	0.00000	-1.07365
O	5.22671	0.00000	-1.11829
O	5.22671	0.00000	1.11829
C	5.83741	0.00000	0.00000
O	3.15848	2.10430	-1.11977
O	3.15848	2.10430	1.11977
C	3.17260	2.71155	0.00000
O	3.15848	-2.10430	1.11977
O	3.15848	-2.10430	-1.11977
C	3.17260	-2.71155	0.00000
H	-6.92984	0.00000	0.00000
H	-3.19566	3.80428	0.00000
H	-3.19566	-3.80428	0.00000
H	6.92984	0.00000	0.00000
H	3.19566	3.80428	0.00000
H	3.19566	-3.80428	0.00000
O	1.10304	0.00000	1.39366
C	0.00000	0.00000	0.75440
C	0.00000	0.00000	-0.75440
O	1.10304	0.00000	-1.39366
O	-1.10304	0.00000	-1.39366
O	-1.10304	0.00000	1.39366

Table S6. Cartesian coordinates of $[W_2]_2$-$\mu(5,5)^0$.

Atom	x	y	z
C	-0.73856	0.00000	0.00000
C	0.73856	0.00000	0.00000
O	1.36740	1.12488	0.00000
O	1.36740	-1.12488	0.00000
W	3.43966	1.10257	0.00000
W	3.43966	-1.10257	0.00000
O	5.55967	1.12587	0.00000
O	5.55967	-1.12587	0.00000
C	6.16129	0.00000	0.00000
H	7.25409	0.00000	0.00000
O	3.46247	1.12522	2.11196
O	3.46247	-1.12522	2.11196
C	3.47152	0.00000	2.71506
H	3.48848	0.00000	3.80737
O	3.46247	-1.12522	-2.11196
O	3.46247	1.12522	-2.11196
C	3.47152	0.00000	-2.71506
H	3.48848	0.00000	-3.80737
O	-1.36740	-1.12488	0.00000
O	-1.36740	1.12488	0.00000
W	-3.43966	-1.10257	0.00000
W	-3.43966	1.10257	0.00000
O	-5.55967	-1.12587	0.00000
O	-5.55967	1.12587	0.00000
C	-6.16129	0.00000	0.00000
H	-7.25409	0.00000	0.00000
O	-3.46247	-1.12522	2.11196
O	-3.46247	1.12522	2.11196
C	-3.47152	0.00000	2.71506
H	-3.48848	0.00000	3.80737
O	-3.46247	1.12522	-2.11196
O	-3.46247	-1.12522	-2.11196
C	-3.47152	0.00000	-2.71506
H	-3.48848	0.00000	-3.80737

Table S7. Cartesian coordinates of $[W_2]_2$-μ(5,5)$^+$.

Atom	x	y	z
C	-0.72524	0.00000	0.00000
C	0.72524	0.00000	0.00000
O	1.36728	1.12890	0.00000
O	1.36728	-1.12890	0.00000
W	3.40909	1.11168	0.00000
W	3.40909	-1.11168	0.00000
O	5.52159	1.12485	0.00000
O	5.52159	-1.12485	0.00000
C	6.12572	0.00000	0.00000
H	7.21778	0.00000	0.00000
O	3.45915	1.12442	2.10301
O	3.45915	-1.12442	2.10301
C	3.48055	0.00000	2.70786
H	3.51795	0.00000	3.79902
O	3.45915	-1.12442	-2.10301
O	3.45915	1.12442	-2.10301
C	3.48055	0.00000	-2.70786
H	3.51795	0.00000	-3.79902
O	-1.36728	-1.12890	0.00000
O	-1.36728	1.12890	0.00000
W	-3.40909	-1.11168	0.00000
W	-3.40909	1.11168	0.00000
O	-5.52159	-1.12485	0.00000
O	-5.52159	1.12485	0.00000
C	-6.12572	0.00000	0.00000
H	-7.21778	0.00000	0.00000
O	-3.45915	-1.12442	2.10301
O	-3.45915	1.12442	2.10301
C	-3.48055	0.00000	2.70786
H	-3.51795	0.00000	3.79902
O	-3.45915	1.12442	-2.10301
O	-3.45915	-1.12442	-2.10301
C	-3.48055	0.00000	-2.70786
H	-3.51795	0.00000	-3.79902

Table S8. Cartesian coordinates of $[W_2]_2$-μ(6,6)^0.

Atom	x	y	z
W	3.14610	1.10332	0.00000
W	3.14610	-1.10332	0.00000
O	5.24748	1.12320	0.00000
O	5.24748	-1.12320	0.00000
C	5.85691	0.00000	0.00000
O	3.15092	1.12495	2.11023
O	3.15092	-1.12495	2.11023
C	3.15389	0.00000	2.71463
O	3.15092	-1.12495	-2.11023
O	3.15092	1.12495	-2.11023
C	3.15389	0.00000	-2.71463
W	-3.14610	1.10332	0.00000
W	-3.14610	-1.10332	0.00000
O	-5.24748	-1.12320	0.00000
O	-5.24748	1.12320	0.00000
C	-5.85691	0.00000	0.00000
O	-3.15092	-1.12495	2.11023
O	-3.15092	1.12495	2.11023
C	-3.15389	0.00000	2.71463
O	-3.15092	1.12495	-2.11023
O	-3.15092	-1.12495	-2.11023
C	-3.15389	0.00000	-2.71463
H	6.94858	0.00000	0.00000
H	3.16030	0.00000	3.80694
H	3.16030	0.00000	-3.80694
H	-6.94858	0.00000	0.00000
H	-3.16030	0.00000	3.80694
H	-3.16030	0.00000	-3.80694
O	-1.09978	1.40891	0.00000
C	0.00000	0.75275	0.00000
C	0.00000	-0.75275	0.00000
O	-1.09978	-1.40891	0.00000
O	1.09978	-1.40891	0.00000
O	1.09978	1.40891	0.00000

Table S9. Cartesian coordinates of $[W_2]_2$-μ(6,6)$^+$.

Atom	x	y	z
W	3.10751	1.11271	0.00000
W	3.10751	-1.11271	0.00000
O	5.20764	1.12250	0.00000
O	5.20764	-1.12250	0.00000
C	5.81677	0.00000	0.00000
O	3.15329	1.12398	2.10265
O	3.15329	-1.12398	2.10265
C	3.17421	0.00000	2.70828
O	3.15329	-1.12398	-2.10265
O	3.15329	1.12398	-2.10265
C	3.17421	0.00000	-2.70828
W	-3.10751	1.11271	0.00000
W	-3.10751	-1.11271	0.00000
O	-5.20764	-1.12250	0.00000
O	-5.20764	1.12250	0.00000
C	-5.81677	0.00000	0.00000
O	-3.15329	-1.12398	2.10265
O	-3.15329	1.12398	2.10265
C	-3.17421	0.00000	2.70828
O	-3.15329	1.12398	-2.10265
O	-3.15329	-1.12398	-2.10265
C	-3.17421	0.00000	-2.70828
H	6.90828	0.00000	0.00000
H	3.21032	0.00000	3.79947
H	3.21032	0.00000	-3.79947
H	-6.90828	0.00000	0.00000
H	-3.21032	0.00000	3.79947
H	-3.21032	0.00000	-3.79947
O	-1.10251	1.40866	0.00000
C	0.00000	0.73703	0.00000
C	0.00000	-0.73703	0.00000
O	-1.10251	-1.40866	0.00000
O	1.10251	-1.40866	0.00000
O	1.10251	1.40866	0.00000

Table S10. Vibrational frequencies (cm^{-1}) for $[Mo_2]_2$-$\mu(5,5)^0$.

43.1	52.3	58.6
72.1	91.1	125.0
128.0	128.4	131.7
145.7	158.4	181.3
184.3	186.9	207.4
224.5	224.6	227.5
231.5	243.8	250.6
283.5	285.0	322.3
324.7	325.6	327.3
348.3	366.3	368.6
372.0	374.7	381.4
386.9	390.5	399.2
399.3	435.5	440.9
441.5	441.8	453.7
456.5	457.2	459.1
460.3	463.7	478.2
479.9	562.2	583.6
604.5	675.9	775.5
777.5	778.1	784.9
786.3	788.4	796.8
800.5	945.1	1003.2
1003.3	1006.1	1006.2
1006.6	1006.6	1331.7
1355.9	1356.1	1357.3
1357.8	1364.7	1366.2
1373.8	1374.2	1374.6
1374.8	1375.1	1375.2
1422.2	1545.1	1550.1
1565.8	1566.6	1569.3
1570.2	1571.2	1572.1
3142.0	3142.0	3142.8
3143.0	3143.5	3143.7

Table S11. Vibrational frequencies (cm^{-1}) for $[Mo_2]_2$-μ(5,5)$^+$.

40.1	50.8	56.2
69.4	92.2	122.9
132.8	135.0	136.3
143.2	159.1	174.0
177.7	184.0	206.2
220.3	222.1	230.2
231.3	240.9	255.8
282.5	285.8	306.6
310.3	312.9	323.5
346.5	353.6	355.8
384.5	386.5	391.3
392.2	392.3	397.6
399.6	429.2	434.0
434.1	438.2	439.3
443.5	449.8	451.3
453.4	458.1	477.7
479.3	564.7	592.8
605.8	677.5	769.3
777.3	778.3	779.5
785.4	787.6	797.2
797.4	945.0	1032.3
1032.3	1033.7	1033.7
1036.6	1036.7	1310.2
1361.2	1361.9	1362.2
1362.3	1363.1	1363.4
1364.2	1364.3	1364.7
1365.1	1371.5	1371.7
1395.6	1486.1	1494.1
1528.0	1528.9	1531.9
1532.0	1537.4	1538.1
3173.0	3173.0	3173.1
3173.2	3175.9	3175.9

Table S12. Vibrational frequencies (cm^{-1}) for $[Mo_2]_2$-$\mu(6,6)^0$.

37.9	51.1	54.9
96.6	106.1	114.3
123.5	127.5	127.8
146.3	155.3	156.8
159.3	179.6	204.2
208.8	209.1	212.5
223.8	234.6	244.3
265.9	276.0	298.1
308.4	315.4	318.2
327.4	369.4	370.8
372.5	373.0	388.6
391.8	393.8	396.2
398.6	404.2	440.2
440.7	444.0	445.0
453.7	459.9	462.8
463.3	463.9	465.3
473.1	477.0	479.5
480.7	602.5	777.4
777.9	785.9	786.0
796.0	797.2	803.7
819.5	971.0	994.1
994.2	1001.8	1002.0
1004.7	1005.0	1351.4
1351.7	1356.2	1356.8
1359.3	1360.4	1362.2
1370.1	1370.2	1372.8
1373.6	1373.9	1374.2
1375.1	1563.3	1565.0
1565.6	1566.2	1569.0
1570.2	1581.5	1620.6
3142.4	3142.6	3142.8
3143.1	3151.3	3151.3

Table S13. Vibrational frequencies (cm^{-1}) for $[Mo_2]_2$-μ(6,6)$^+$.

37.2	50.1	55.3
97.6	106.5	119.3
121.1	136.7	137.1
146.0	156.6	164.7
165.9	176.0	203.1
207.1	207.6	232.0
233.6	241.7	245.4
266.9	285.1	296.2
301.0	304.9	313.9
320.9	353.4	360.8
385.3	388.3	397.0
397.7	397.9	401.9
408.4	420.4	434.2
435.2	435.4	439.9
440.7	443.0	452.0
454.1	458.4	458.6
471.5	474.9	484.2
485.5	613.7	778.0
778.8	786.9	787.1
791.4	796.2	798.0
814.2	983.8	1031.7
1031.7	1032.3	1032.3
1033.3	1033.4	1323.9
1324.0	1353.2	1357.6
1360.3	1360.9	1363.0
1363.4	1364.3	1364.8
1365.4	1366.4	1371.8
1375.8	1484.8	1486.6
1511.1	1530.7	1531.9
1539.9	1541.0	1541.9
3172.3	3172.4	3172.5
3172.6	3181.2	3181.2

Table S14. Vibrational frequencies (cm^{-1}) for $[W_2]_2$-$\mu(5,5)^0$.

41.0	48.8	56.0
64.7	84.8	118.3
122.9	123.2	126.2
126.8	152.4	201.6
204.9	205.0	213.0
227.3	229.4	229.5
233.2	249.4	250.7
293.7	293.8	297.7
299.9	308.9	316.3
336.8	339.8	368.0
373.5	376.1	376.3
377.7	389.7	393.7
396.7	405.3	423.9
437.1	443.2	454.3
454.5	470.1	470.8
471.8	474.9	504.3
505.3	594.5	596.2
609.5	704.5	748.7
769.0	774.6	774.9
784.4	789.4	798.5
801.3	940.6	970.6
970.6	975.4	975.7
979.1	979.1	1289.5
1325.9	1326.4	1326.8
1327.1	1337.8	1341.6
1371.1	1371.6	1371.8
1372.0	1373.2	1373.2
1390.2	1487.8	1494.7
1549.5	1549.8	1550.2
1550.3	1552.6	1553.7
3159.1	3159.1	3162.9
3163.0	3163.7	3163.8

Table S15. Vibrational frequencies (cm^{-1}) for $[W_2]_2$-μ(5,5)$^+$.

37.3	46.6	52.8
61.2	87.3	116.3
125.1	128.1	129.1
132.6	156.7	188.1
192.4	204.3	211.1
226.0	228.5	230.2
234.0	246.6	255.1
274.5	279.8	281.0
281.4	300.9	322.4
334.0	337.5	360.0
369.4	375.7	394.3
394.6	398.4	399.8
410.4	411.1	412.5
420.0	422.9	424.2
448.2	448.3	455.0
463.5	468.5	502.4
503.9	606.0	606.9
612.0	713.0	738.1
761.5	776.1	776.7
786.2	789.4	799.9
800.8	926.0	1018.5
1018.5	1020.4	1020.5
1027.9	1028.0	1268.3
1345.7	1345.8	1346.4
1346.7	1355.3	1358.3
1363.1	1363.5	1364.8
1365.2	1365.9	1366.3
1398.5	1419.0	1430.2
1523.5	1523.8	1528.0
1528.8	1535.9	1537.3
3183.9	3183.9	3185.6
3185.7	3186.0	3186.0

Table S16. Vibrational frequencies (cm^{-1}) for $[W_2]_2$-$\mu(6,6)^0$.

38.2	47.2	53.2
92.3	104.6	109.4
117.4	122.4	122.9
130.1	158.1	161.0
178.2	198.5	216.0
217.0	218.4	224.0
229.0	237.2	244.2
264.4	287.6	295.5
295.8	299.9	300.8
301.0	339.4	346.5
373.7	374.7	383.8
386.5	392.6	393.2
399.9	409.3	411.3
426.6	450.1	451.5
454.6	455.0	473.2
473.9	478.9	481.6
485.1	486.5	506.5
507.9	618.6	772.3
773.8	774.2	784.9
785.0	797.5	798.2
824.6	953.1	953.3
966.2	966.5	970.1
970.2	986.7	1281.1
1314.9	1315.1	1322.1
1322.5	1329.1	1334.1
1338.5	1365.3	1365.5
1369.6	1370.4	1370.6
1371.1	1523.9	1541.9
1543.5	1546.9	1547.5
1548.1	1548.7	1550.8
3163.6	3163.7	3164.3
3164.5	3172.0	3172.0

Table S17. Vibrational frequencies (cm^{-1}) for $[W_2]_2$-μ(6,6)$^+$.

37.3	45.5	52.9
94.9	107.7	114.6
114.8	131.0	132.2
133.3	160.8	163.4
190.3	191.3	212.8
215.7	218.3	232.2
236.9	245.3	248.0
257.8	273.2	278.4
286.5	287.3	297.7
310.8	337.2	350.8
367.1	372.7	398.6
399.2	400.1	402.3
414.5	414.9	419.5
423.9	429.1	429.2
433.3	449.3	449.5
469.7	474.6	478.7
489.7	503.1	504.2
506.0	639.0	752.9
776.0	776.7	787.2
787.3	798.6	799.6
821.8	993.1	1016.1
1016.2	1018.4	1018.5
1019.2	1019.3	1272.8
1290.9	1342.2	1342.7
1344.4	1345.1	1353.9
1358.6	1359.9	1360.3
1362.3	1363.8	1364.8
1365.3	1441.8	1462.4
1524.1	1524.3	1525.0
1528.9	1529.7	1530.0
3185.4	3185.5	3185.7
3185.8	3191.1	3191.1