Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Electronic Supporting Information for

Nonclassical oxygen atom transfer reactions of an eight-coordinate dioxomolybdenum(VI) complex

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I. Crystallographic details for $MoO_2(DOPO^Q)$

Table S1. Crystal data for $MoO_2(DOPO^Q)_2$.

Empirical formula	$C_{56}H_{76}N_2O_8Mo$
Formula weight	1001.13
Temperature / *K*	120(2)
Crystal system	Monoclinic
Space group	$P2_1/n$
a / Å	20.2266(16)
b / Å	27.459(2)
c / Å	20.4708(16)
α / °	90
β / °	110.0796(19)
γ / °	90
Volume / $Å^3$	10678.6(15)
Z	8
ρ_{calc} / g cm^{-3}	1.245
μ / mm^{-1}	0.299
F(000)	4256
Crystal size / mm^3	0.11 × 0.09 × 0.07
2θ range for data collection	2.96 to 41.86°
Reflections collected	131390
Independent reflections	11361 [R_{int} = 0.1942]
Data/restraints/parameters	11361/6/1255
Goodness-of-fit on F^2	0.987
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0468, $wR2$ = 0.0877
Final R indices [all data]	$R1$ = 0.0909, $wR2$ = 0.0991

Figure S1. Thermal ellipsoid plots (50% ellipsoids) of the two inequivalent molecules of $MoO_2(DOPO^Q)_2$ in the crystal. Hydrogen atoms are omitted for clarity. (a) Molecule 1; (b) molecule 2.

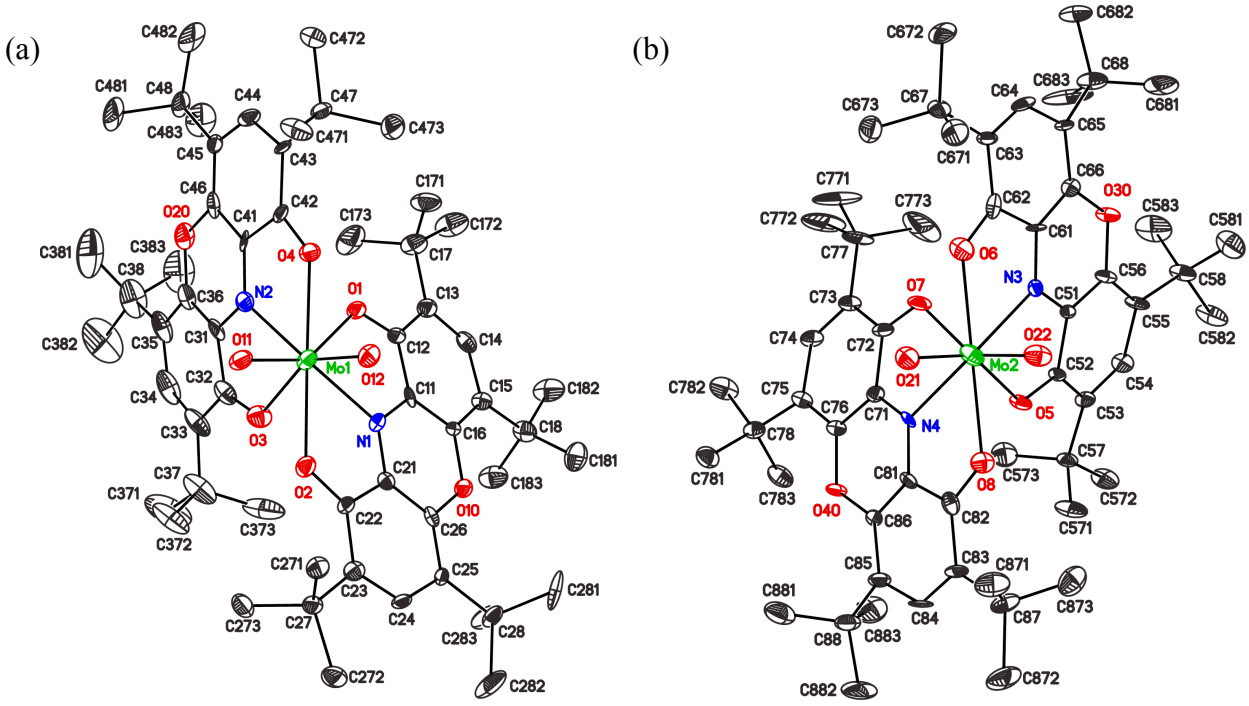


Table S2. Selected distances (Å) for $MoO_2(DOPO^Q)_2$.

Distance[a]	*Molecule 1*		*Molecule 2*		***Average***
Mo1–O1	2.247(3)	2.247(3)	2.255(3)	2.294(3)	**2.261(23)**
Mo1–O2	2.333(3)	2.312(3)	2.296(3)	2.305(3)	**2.312(16)**
Mo1–N1	2.357(4)	2.332(4)	2.346(4)	2.362(4)	**2.350(13)**
Mo1–O11	1.687(3)	1.684(3)	1.691(3)	1.689(3)	**1.688(4)**
C11–N1	1.333(6)	1.333(6)	1.325(6)	1.331(6)	**1.331(7)**
C12–O1	1.298(6)	1.282(6)	1.275(5)	1.279(6)	**1.284(12)**
C11–C12	1.421(7)	1.423(7)	1.431(6)	1.436(7)	**1.428(10)**
C12–C13	1.416(7)	1.419(7)	1.420(7)	1.414(7)	**1.417(8)**
C13–C14	1.381(7)	1.392(8)	1.377(7)	1.366(6)	**1.379(13)**
C14–C15	1.421(7)	1.412(8)	1.434(7)	1.422(6)	**1.422(11)**
C15–C16	1.376(7)	1.376(7)	1.363(7)	1.361(6)	**1.369(11)**
C11–C16	1.408(7)	1.412(7)	1.413(7)	1.416(7)	**1.412(8)**
C21–N1	1.316(6)	1.329(6)	1.315(5)	1.324(6)	**1.321(9)**
C22–O2	1.273(5)	1.276(5)	1.273(6)	1.275(6)	**1.274(6)**
C21–C22	1.449(7)	1.446(7)	1.438(7)	1.429(7)	**1.441(11)**
C22–C23	1.428(7)	1.410(7)	1.433(7)	1.434(7)	**1.426(13)**
C23–C24	1.374(7)	1.388(7)	1.377(7)	1.364(7)	**1.376(12)**
C24–C25	1.441(7)	1.412(7)	1.429(7)	1.434(7)	**1.429(14)**
C25–C26	1.360(6)	1.358(7)	1.366(6)	1.360(6)	**1.361(8)**
C21–C26	1.424(7)	1.436(7)	1.415(7)	1.404(7)	**1.420(15)**

[a]Numbering is given for molecule 1, ring 1 (which is equivalent to rings 3, 5, and 7, which are listed in successive columns) or for molecule 1, ring 2 (which is equivalent to rings 4, 6, and 8, listed in successive columns). Metal-oxo distances are listed in order O11, O12, O21, O22.

Table S3. Selected angles (º) for $MoO_2(DOPO^Q)_2$.

Angle[a]	*Molecule 1*		*Molecule 2*		***Average***
O11–Mo1–O12	104.50(16)		105.50(16)		**105.0(7)**
O11–Mo1–O1	144.78(13)	145.80(14)	144.99(14)	145.77(14)	**145.3(5)**
O11–Mo1–O2	79.59(13)	78.18(14)	78.45(14)	77.87(14)	**78.5(8)**
O11–Mo1–O3	91.08(14)	94.24(14)	93.67(14)	93.66(14)	**93.2(14)**
O11–Mo1–O4	84.26(13)	82.46(13)	84.64(14)	85.52(14)	**84.2(13)**
O11–Mo1–N1	144.48(16)	143.67(16)	143.70(15)	142.88(15)	**143.7(7)**
O11–Mo1–N2	82.75(14)	81.35(15)	82.08(14)	80.98(14)	**81.8(8)**
O1–Mo1–O2	133.09(12)	134.43(12)	133.03(13)	132.96(12)	**133.4(7)**
O1–Mo1–O3	89.60(12)		85.79(12)		**88(3)**
O1–Mo1–O4	70.55(12)	70.47(12)	70.87(12)	70.62(12)	**70.6(2)**
O1–Mo1–N1	66.94(14)	67.40(15)	67.20(13)	66.67(13)	**67.1(3)**
O1–Mo1–N2	65.14(13)	68.99(13)	65.56(12)	67.25(12)	**66.7(18)**
O2–Mo1–O4	150.75(11)		152.19(12)		**151.5(10)**
O2–Mo1–N1	66.30(14)	67.04(14)	66.31(14)	66.55(13)	**66.6(3)**
O2–Mo1–N2	133.67(14)	130.80(14)	131.36(13)	131.19(13)	**131.8(13)**
N1–Mo1–N2	113.47(15)		114.55(14)		**114.0(8)**

[a]Numbering is given for molecule 1.

II. NMR spectra of $MoO_2(DOPO^Q)_2$

Figure S2. ^1H NMR spectrum of $MoO_2(DOPO^Q)_2$ (CD_2Cl_2, 400 MHz, 23 °C). Assignments: δ 0.91, 1.40, 1.41, 1.49 (s, 18H each, ^{t}Bu), 7.39, 7.62 (s, 2H each, Ar*H*). The solvent residual signal is marked with a *.

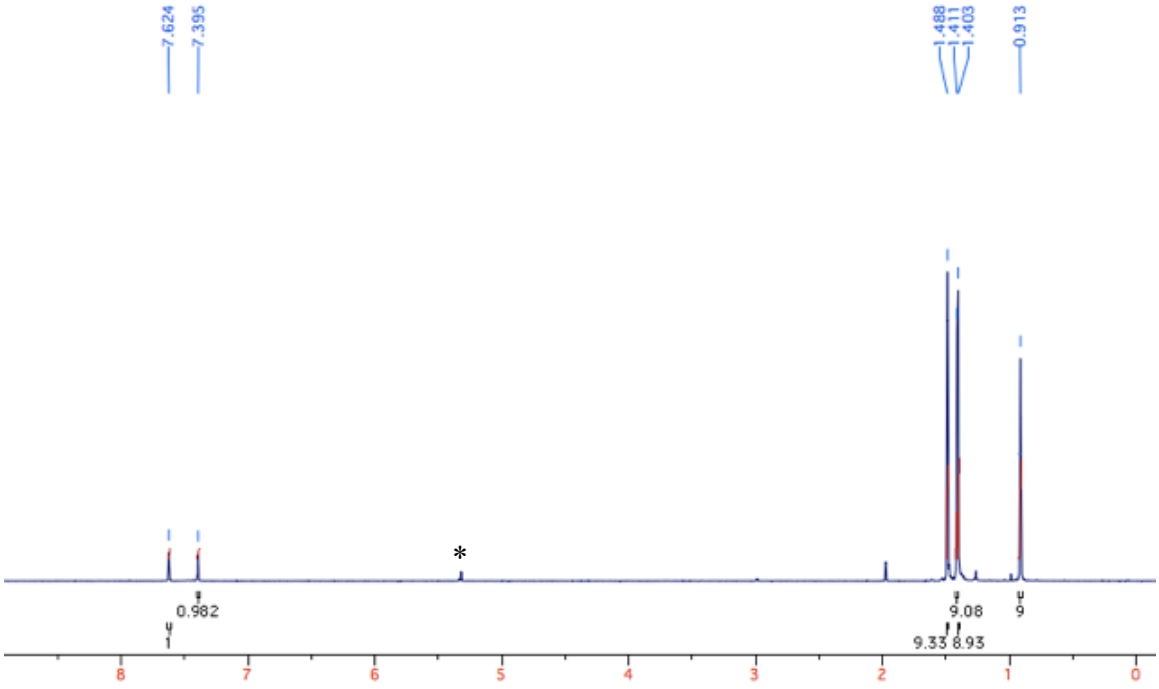
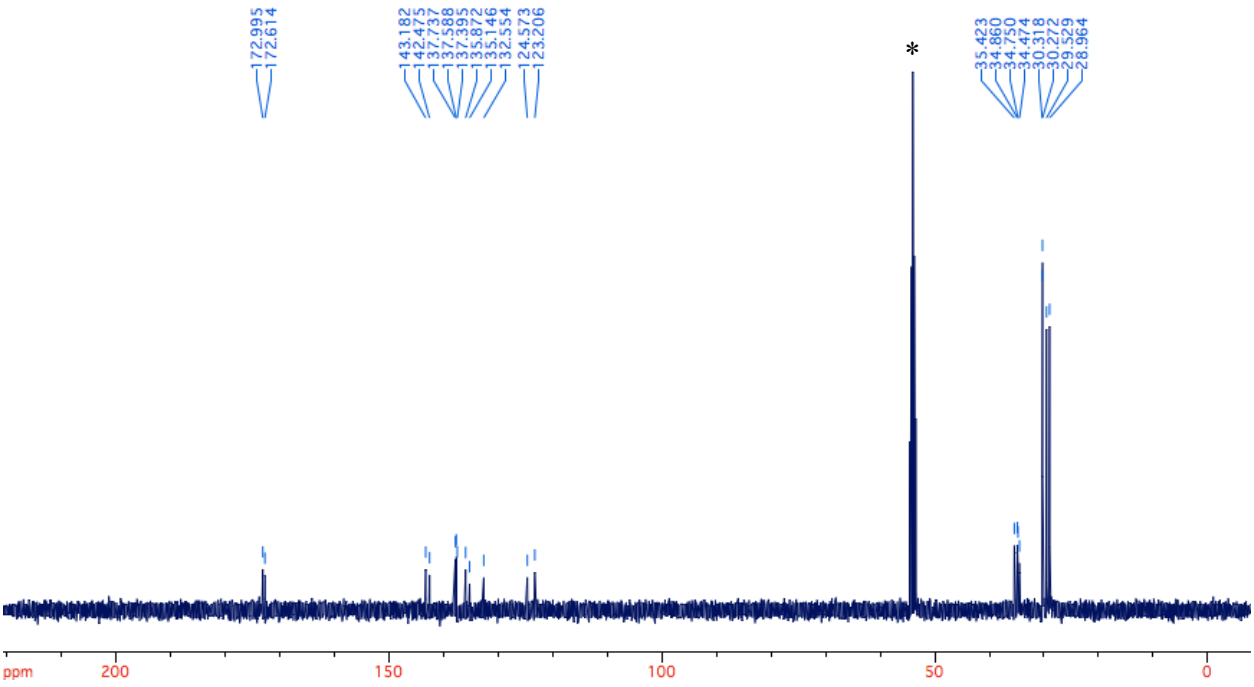
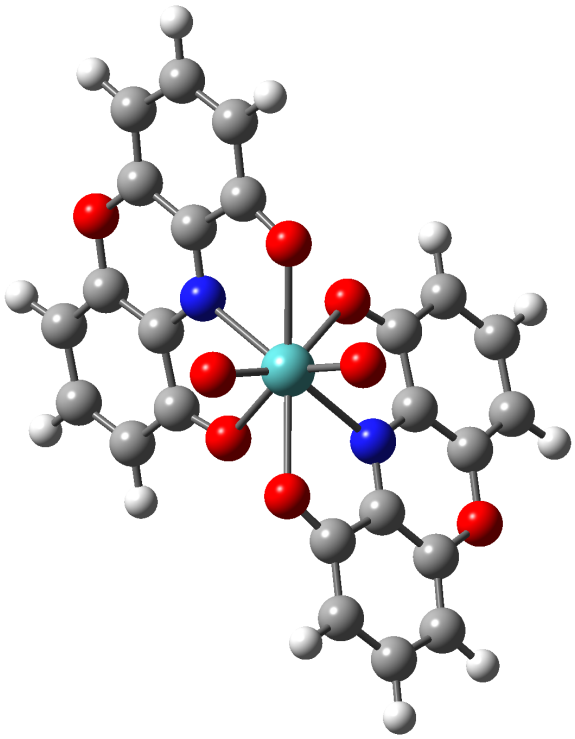


Figure S3. $^{13}C\{^{1}H\}$ NMR spectrum of $MoO_2(DOPO^{Q})_2$ (CD_2Cl_2, 100.6 MHz, 23 °C). Assignments: δ 29.0, 29.5, 30.26, 30.31 ($C(CH_3)_3$); 34.5, 34.8, 34.9, 35.4 ($C(CH_3)_3$); 123.2, 124.6, 132.6, 135.1, 135.9, 137.4, 137.6, 137.7, 142.5, 143.2 (aromatics); 172.6, 173.0 (*C*OMo).. The *C*D_2Cl_2 signal is marked with a *.



III. Computational details for $MoO_2(DOPO^Q)_2$



Optimized energy = –1701.35681778 a. u.
Cartesian coordinates:

Center Number	Atomic Number	Coordinates (Å) X	Y	Z
1	42	-0.025443	0.000000	0.000000
2	8	-1.056987	1.354785	-0.057625
3	8	1.717639	1.100812	-1.208403
4	8	-0.581983	-0.062375	2.272318
5	8	2.605443	3.397325	2.842444
6	7	1.254935	1.505820	1.319995
7	6	2.178417	2.271461	0.756164
8	6	2.406916	2.019699	-0.648765
9	6	3.401396	2.832544	-1.264012
10	1	3.617136	2.700431	-2.318596
11	6	4.069147	3.781122	-0.506353
12	1	4.822006	4.393024	-0.996990
13	6	3.843274	4.017021	0.879209
14	1	4.400370	4.772612	1.420415
15	6	2.891473	3.251074	1.507042
16	6	0.975625	1.639986	2.600387
17	6	-0.048126	0.740515	3.098036
18	6	-0.348826	0.859035	4.488088
19	1	-1.104970	0.215040	4.922716
20	6	0.324746	1.796980	5.247518
21	1	0.078056	1.875752	6.303374
22	6	1.329443	2.681414	4.749497

23	1	1.820098	3.395899	5.399900
24	6	1.650543	2.595203	3.419884
25	8	-1.056987	-1.354785	0.057625
26	8	1.717639	-1.100812	1.208403
27	8	-0.581983	0.062375	-2.272318
28	8	2.605443	-3.397325	-2.842444
29	7	1.254935	-1.505820	-1.319995
30	6	2.178417	-2.271461	-0.756164
31	6	2.406916	-2.019699	0.648765
32	6	3.401396	-2.832544	1.264012
33	1	3.617136	-2.700431	2.318596
34	6	4.069147	-3.781122	0.506353
35	1	4.822006	-4.393024	0.996990
36	6	3.843274	-4.017021	-0.879209
37	1	4.400370	-4.772612	-1.420415
38	6	2.891473	-3.251074	-1.507042
39	6	0.975625	-1.639986	-2.600387
40	6	-0.048126	-0.740515	-3.098036
41	6	-0.348826	-0.859035	-4.488088
42	1	-1.104970	-0.215040	-4.922716
43	6	0.324746	-1.796980	-5.247518
44	1	0.078056	-1.875752	-6.303374
45	6	1.329443	-2.681414	-4.749497
46	1	1.820098	-3.395899	-5.399900
47	6	1.650543	-2.595203	-3.419884