ELECTRONIC SUPPLEMENTARY INFORMATION

Olefin epoxidation by hydrogen peroxide catalysed by molybdenum complexes in ionic liquids and structural characterisation of the proposed intermediate dioxoperoxomolybdenum species

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Experimental details

Reactions were performed under a dry, oxygen-free, nitrogen atmosphere using standard Schlenk techniques, unless otherwise stated. All solvents were dried and degassed appropriately before use. Chemicals were obtained from commercial sources and used as supplied. Ionic liquids $C_n$mim-PF_6 were prepared according to literature procedures.[1] Infrared spectra were recorded on a Perkin-Elmer Model 883 spectrophotometer (as either liquid film supported on KBr discs or in pressed KBr pellets). NMR spectra were recorded using a Bruker AMX-300 spectrometer with $^{13}C\{^1H\}$ and ^1H shifts referenced to the residual solvent signals. All data are reported in ppm downfield from Me_4Si. Gas chromatography was carried out using a Varian CP-3800. Elemental analysis (C, H, N) were performed on an Elemental LECO CHNS 93 analyser by the Microanalytical Service of the Universidad de Sevilla (CITIUS).

Synthesis of $[Mo_4O_{16}(dmpz)_6]$ (1)

Solutions of 440 mM aqueous $[Mo(O)(O_2)_2(H_2O)_n]$[2] (2 mL, 0.877 mmol) and 3,5-dimethylpyrazole (170 mg, 1.75 mmol) in dichloromethane (5 mL) were stirred together for 30 minutes. Stirring was then discontinued, observing the formation of a biphasic system wherein the yellow colouration previously resident in the aqueous phase had now transferred in large part to the organic. The latter was subsequently separated, dried ($MgSO_4$), filtered and transferred to a small test tube which was sealed and stored at -15 ºC in a freezer. After several months the formation of crystals in a viscous orange oil was observed. The crystals were separated, washed with cold acetone and dried in air. The product was thus obtained as relatively large orange crystals as dichloromethane solvate **1**·CH_2Cl_2 (32 mg, 0.026 mmol, 12

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1 (a) S. Carda-Broch, A. Berthod and D. W. Armstrong, *Anal. Bioanal. Chem.*, 2003, **375**, 191; (b) C. M. Gordon, J. D. Holbrey, A. R. Kennedy and K. R. Seddon, *J. Mater. Chem.*, 1998, **8**, 2627.

2 Prepared by dissolving MoO_3 in excess 30 % aqueous H_2O_2 at 55 ºC. Note that the resultant solutions are actually composed of various molybdenum species in equilibrium dependent on factors including concentration pH and temperature. See for example: (a) L. J. Csáinyi, *Transit. Metal Chem.*, 1989, **14**, 298. (b) L. J. Csanyi, I. Horvath and Z. M. Galbacs, *Transit. Metal Chem.*, 1989, **14**, 90. (c) E. Richardson, *J. Less-Common Met.,* 1960, **2**, 360. (d) G. M. Vol'dman, E. A. Mironova and L. V. Bystrov, *Zh. Neorg. Khim+.*, 1990, **35**, 1306.

%). IR (KBr, cm^{-1}): 631, 668, 745, 853, 903, 956, 967, 1027, 1051, 1151, 1180, 1272, 1299, 1374, 1410, 1472, 1572, 1616, 2856, 2926, 3132, 3420. Calc. Anal. for $Mo_4C_{31}H_{50}N_{12}O_{16}Cl_2$: C, 28.61; H, 3.87; N, 12.91. Found: C, 28.50; H, 4.25; N, 12.67 %.

Synthesis of $[Mo(O)(O_2)_2(pz)_2]$ (2)

A solution of $[Mo(O)(O)_2(H_2O)_n]$ was produced by reaction of MoO_3 (5.00 g, 34.7 mmol) with 30 % aqueous hydrogen peroxide (14 equiv., 50 mL, 490 mmol) at 55 ºC for 1 h. Pyrazole (2 equiv., 4.72 g, 69.4 mmol) was then slowly added over 30 minutes whilst the solution was stirred at 0 ºC. The mixture was then stirred for several hours at 0 ºC before the resulting microcrystalline yellow solid was isolated by filtration (5.72 g, 16.6 mmol, 48 % yield). From the solution, crystals of **2**, suitable for X-ray studies, formed slowly over two days at room temperature. IR (KBr, cm^{-1}): 535, 580, 608, 652, 714, 762, 789, 852, 875, 912, 963, 1044, 1055, 1076, 1128, 1146, 1172, 1254, 1284, 1355, 1399, 1466, 2818, 2875, 2924, 2989, 3042, 3127, 3148, 3328. Calc. Anal. for $MoC_6H_8O_5N_4$: Mo, 30.74; C, 23.09; H, 2.58; N, 17.95. Found: Mo, 29.05; C, 22.27; H, 2.58; N, 18.02 %.

Synthesis of $[Mo(O)(O_2)_2(dmpz)_2]$ (3)

Following the same experimental procedure as that employed in the synthesis of $[Mo(O)(O_2)_2(pz)_2]$, but adding 3,5-dimethylpyrazole in place of pyrazole, the product was obtained as a yellow microcrystalline solid (6.76 g, 18.4 mmol, 53 %). The product appears to decompose, darkening considerably within several days. This process can be slowed, but not prevented, by storing the product under nitrogen at low temperature. IR (KBr, cm^{-1}): 532, 586, 659, 668, 701, 742, 815, 860, 878, 957, 1023, 1040, 1061, 1096, 1150, 1230, 1276, 1413, 1576, 2872, 2929, 2973, 3039, 3140, 3206, 3325. Calc. Anal. for $MoC_{10}H_{16}O_5N_4$: Mo, 26.06; C, 32.62; H, 4.38; N, 15.22. Found: Mo, 24.05; C, 32.01; H, 4.36; N, 14.54 %.

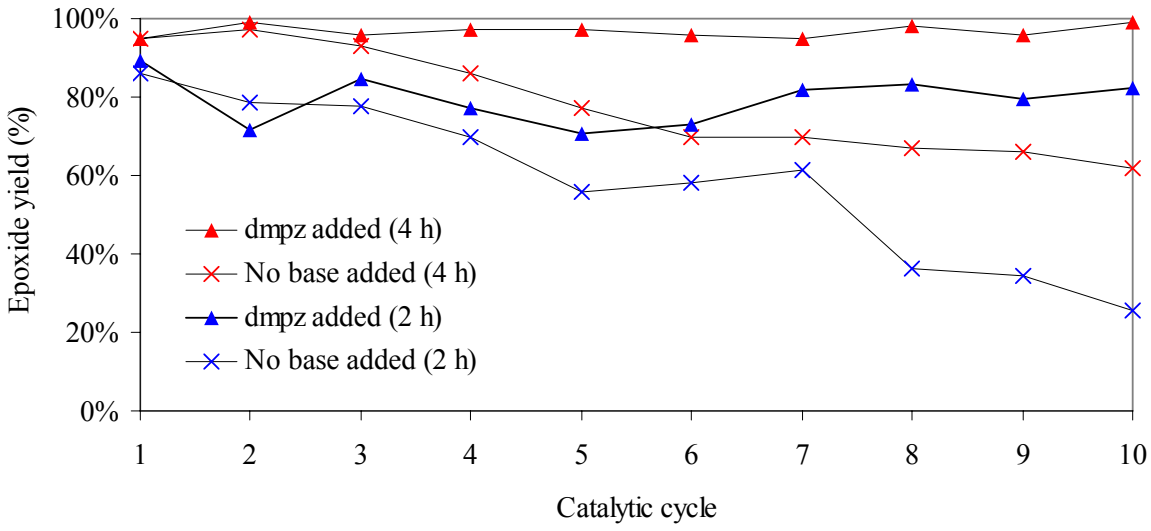
General catalytic procedure for the olefin epoxidation

The reactor (a 50 mL vial equipped with a Young valve and containing a stirrer flea) was charged with 0.5 M aqueous $[Mo(O)(O)_2(H_2O)_n]$ (50 µL, 0.025 mmol), N-donor base additive (0.1 mmol), reaction solvent (2 mL), 30 % aqueous hydrogen peroxide (350 µL, 3

mmol) and the olefin substrate (1 mmol) in the aforementioned order. The reactor was sealed and heated at 60 ºC, maintaining constant stirring in a thermostatted oil bath over 4 h. After the reaction time was complete the reactor was immediately cooled to 0º C and the products extracted with petroleum ether (3 x 3 mL). The resulting solution was dried ($MgSO_4$) and analysed by GC.

Recycling the [Mo]/IL mixture

To investigate the efficiency of catalyst immobilisation in the IL phase in the C_8mim-PF_6/dmpz system, parallel catalytic studies were carried out wherein the IL and immobilised catalyst were recycled in further catalytic cycles. Studies were run with both 4 h cycles, which give effectively complete conversion on the first cycle thus allowing assessment of the maximum achievable TONs, and 2 h cycles, which give incomplete conversion and permit clearer analysis of changes in catalytic efficiency. In each case the importance of refreshing the base additive in between cycles was also investigated. Up to the product extraction the experimental procedure for each cycle was conducted as detailed above. Afterwards the reactor was stirred and heated at 60 ºC under vacuum for around 30 minutes to remove any volatile residues remaining in the reaction mixture. The reactor was then cooled and 30 % aqueous hydrogen peroxide (350 µL, 3 mmol) and olefin substrate (1 mmol) were again charged to the reactor, which was sealed before repeating the epoxidation reaction in the manner detailed above. In the specified experiments 3,5-dimethylpyrazole (0.1 mmol) was also added between cycles at the same time as the oxidant and substrate.



Computational details

The electronic structure and geometries of the model compounds were computed using density functional theory at the B3LYP level.[3,4] The Mo atom was described with the LANL2DZ basis set[5,6] while the 6-31G(d,p) basis set was used for the C, O, N and H atoms. The DFT calculations were performed using the Gaussian 03 suite of programs.[7] The nature of the optimised geometries of all the compounds were characterised by the calculated number of imaginary frequency at the same level of theory, *i.e.*, energy minimum structures without imaginary frequencies (NImag=0). Transition states $\mathbf{TS_1}$ and $\mathbf{TS_2}$ were located using the quadratic synchronous transit (QST2) approach[8] and frequency calculations were performed in order to check the stationary states (NImag=1).

3 A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648.
4 C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785.
5 T. H. Dunning, Jr. and P. J. Hay, *Modern Theoretical Chemistry*, Plenum, New York, 1976, p. 1.
6 P. J. Hay and W. R. Wadt, *J. Chem. Phys.*, 1985, **82**, 299.
7 Gaussian 03, Revision C.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez,, J. A. Pople, Gaussian, Inc., Wallingford CT, 2004.
8 C. Peng, P. Ayala, H. Schlegel and M. Frisch, *J. Comput. Chem.*, 1996, **17**, 49.

Fig. S1 Colour changes during stoichiometric epoxidation with $[Mo(O)(O_2)_2(pz)_2]$.

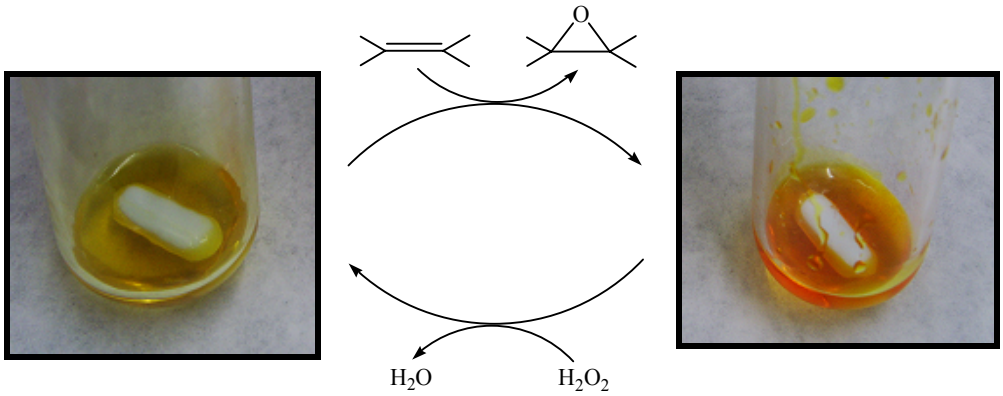


Fig. S2 Energy profile for the model epoxidation reaction with $[Mo(O)(O_2)_2(dmpz)]$ showing the formation of the intermediate dioxoperoxo **C**, with zero point corrected electronic energies and Gibbs free energies (*italics*) (kcal mol^{-1}).

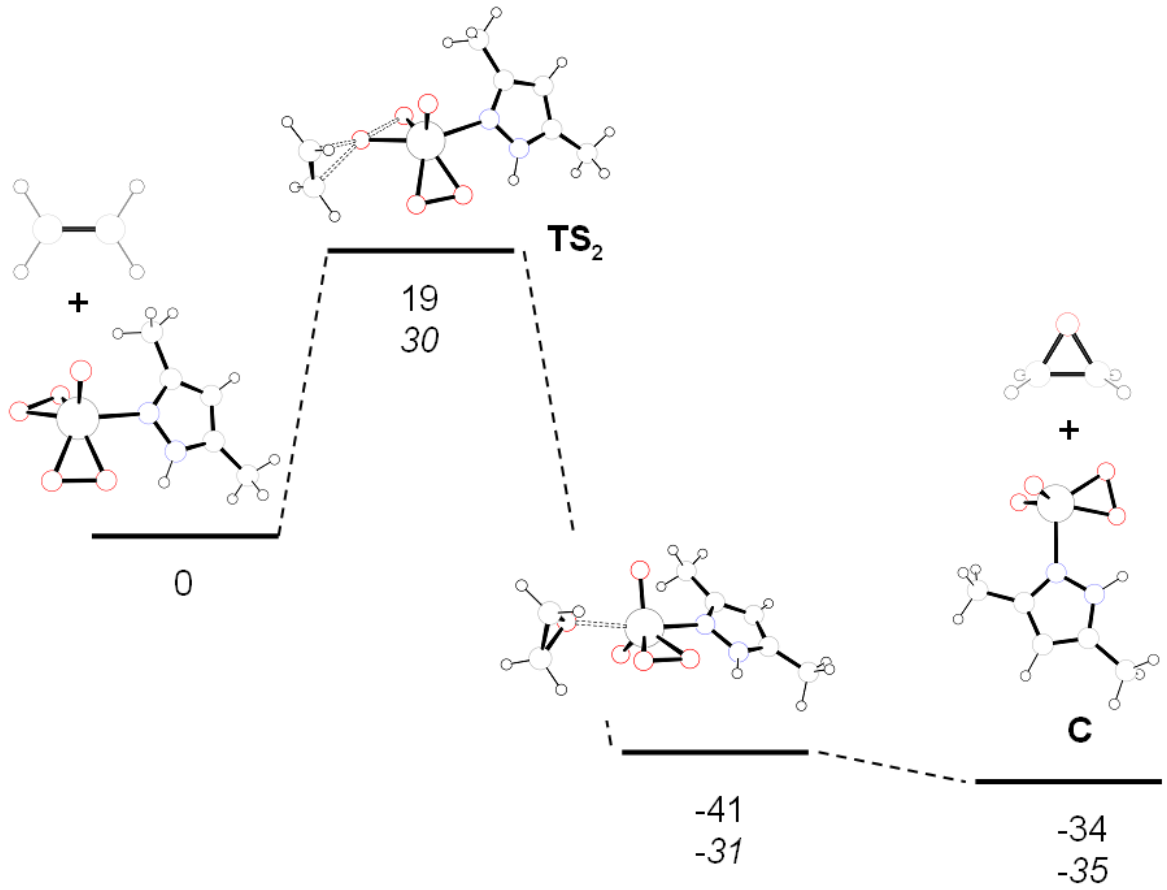


Fig. S3 Selected structural parameters of the optimised transition structures $\mathbf{TS_1}$ and $\mathbf{TS_2}$.

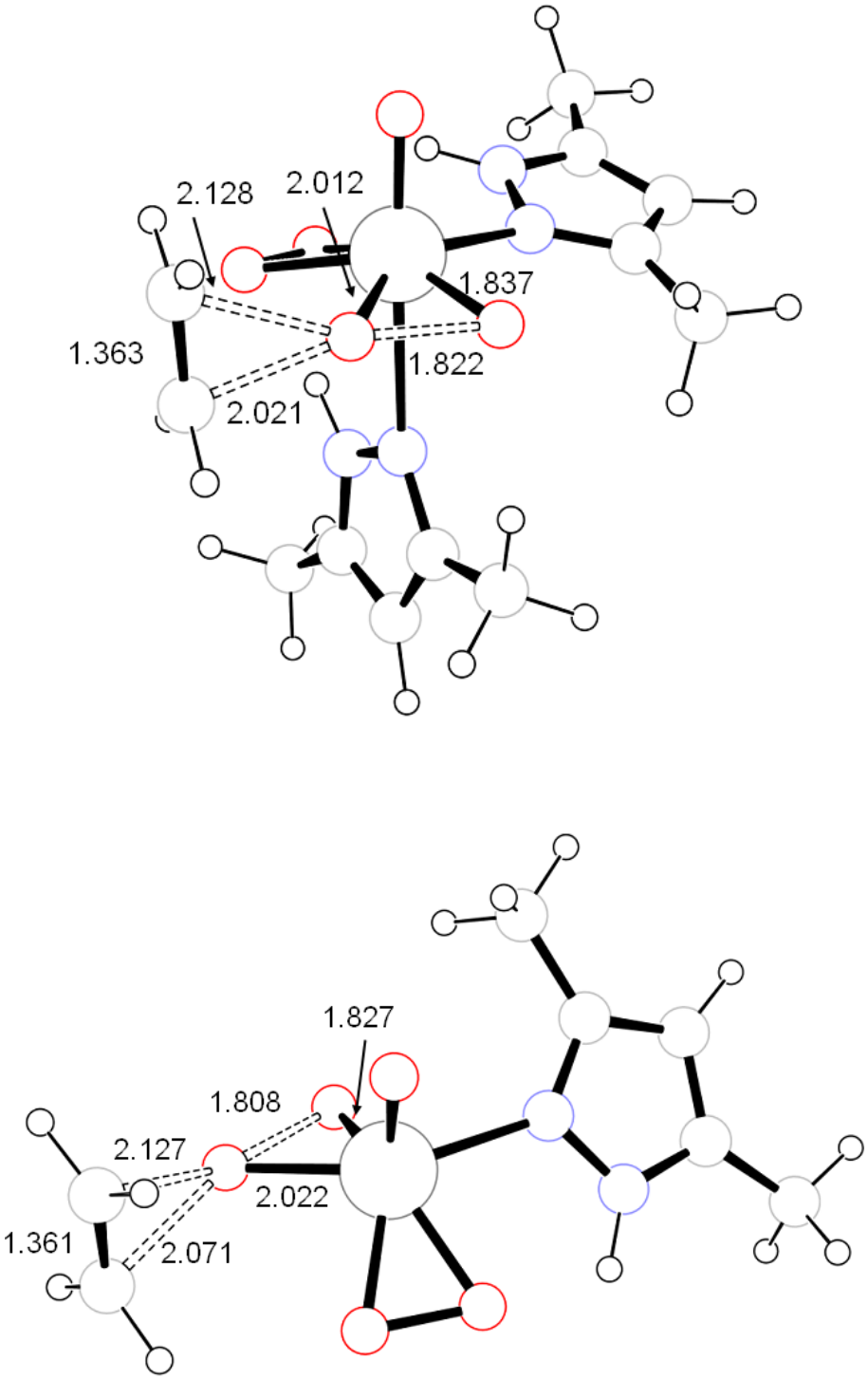
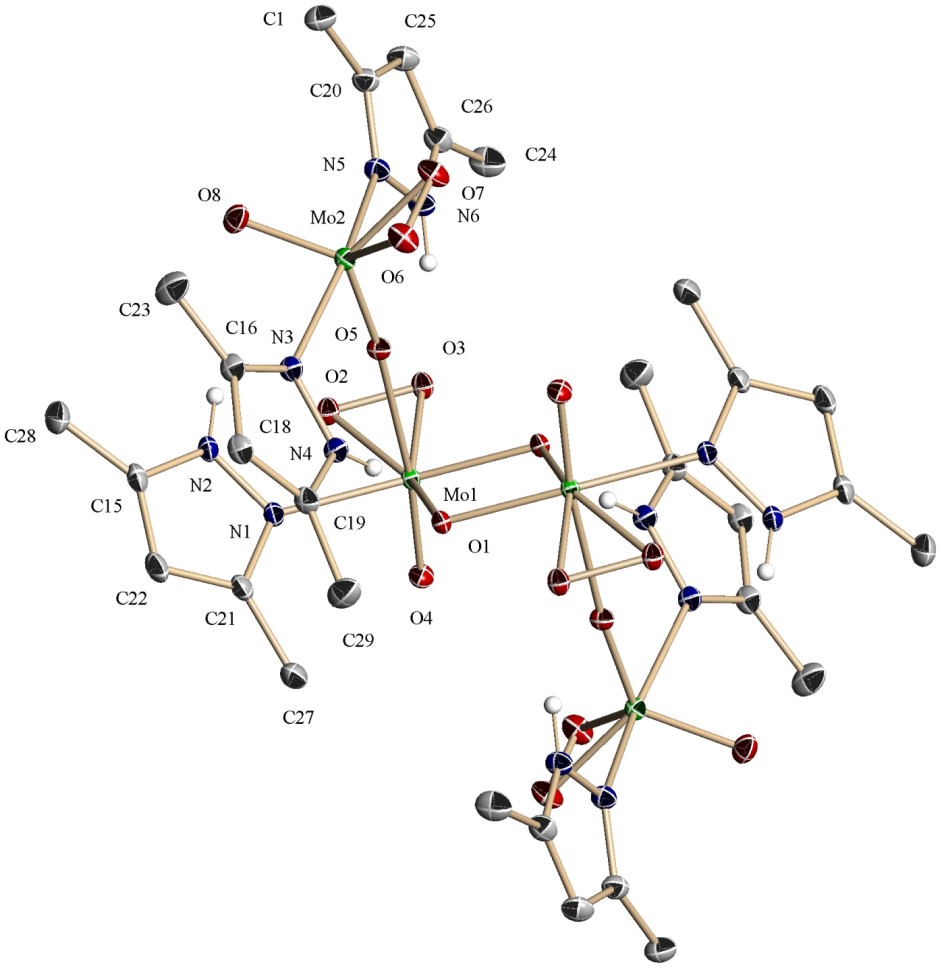


Fig. S4 X-ray structures of $[Mo_4O_{16}(dmpz)_6]$ (**1**) and $[Mo(O)(O_2)_2(pz)_2]$ (**2**) (30 % probability thermal ellipsoids; H atoms have been omitted for clarity).



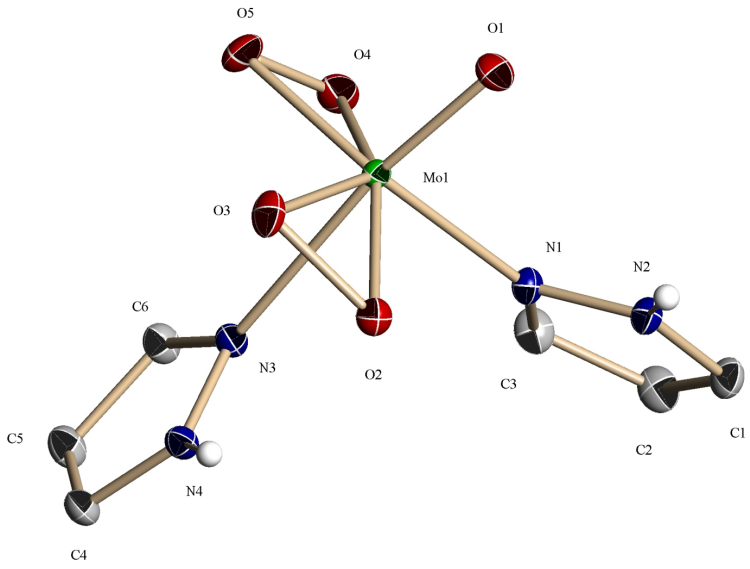


Table S1 Selected bond distances (Å) and angles (º) in experimental $[Mo_4O_{16}(dmpz)_6]$ (**1**) and calculated $[Mo_4O_{16}(dmpz)_6]$, $[Mo(O)_2(O_2)(dmpz)_2]$ and $[Mo_2O_8(dmpz)_2]$.

Experimental		**Calculated**			
$[Mo_4O_{16}(dmpz)_6]$			$[Mo_4O_{16}(dmpz)_6]$	$[Mo(O)_2(O_2)(dmpz)_2]$	$[Mo_2O_8(dmpz)_2]$
Mo(1)-O(1)	1.942(15)	Mo-O	1.948		1.876
Mo(1)-O(2)	1.9560(16)	Mo-O	1.976		1.952
Mo(1)-O(3)	1.9547(16)	Mo-O	1.989		1.952
Mo(1)-O(4)	1.6760(16)	Mo=O	1.693		1.703
Mo(1)-O(5)	2.3455(15)	Mo-O	2.534		
Mo(1)-O(1)#1	1.9597(14)	Mo-O	1.998		2.037
Mo(1)-N(1)	2.1979(18)	Mo-N	2.247		2.271
O(2)-O(3)	1.447(2)	O-O	1.426		1.426
Mo(2)-O(8)	1.7072(17)	Mo=O	1.731	1.724	
Mo(2)-O(5)	1.7633(15)	Mo=O	1.779	1.777	
Mo(2)-O(6)	1.9240(17)	Mo-O	1.954	1.959	
Mo(2)-O(7)	1.9255(17)	Mo-O	1.954	1.959	
Mo(2)-N(3)	2.2066(19)	Mo-N	2.250	2.252	
Mo(2)-N(5)	2.207(2)	Mo-N	2.255	2.252	
O(6)-O(7)	1.451(2)	O-O	1.425	1.429	
O(1)#1-Mo(1)-N(1)	154.77(7)	O-Mo-N	155.2		155.7
O(4)-Mo(1)-O(5)	173.24(7)	O-Mo-O	169.7		
O(8)-Mo(2)-O(5)	118.19(8)	O=Mo=O	115.5	117.7	
N(3)-Mo(2)-N(5)	163.66(7)	N-Mo-N	164.8	159.6	

Table S2 Selected bond distances (Å) and angles (º) in $[Mo(O)(O_2)_2(pz)_2]$ (**2**).

Mo(1)-O(1)	1.6778(12)	O(3)-Mo(1)-O(4)	133.79(6)
Mo(1)-O(2)	1.9620(12)	O(1)-Mo(1)-O(2)	100.53(6)
Mo(1)-O(3)	1.9357(12)	O(5)-Mo(1)-O(2)	133.46(6)
Mo(1)-O(4)	1.9401(13)	O(3)-Mo(1)-O(2)	44.65(5)
Mo(1)-O(5)	1.9189(13)	O(4)-Mo(1)-O(2)	155.36(5)
Mo(1)-N(1)	2.1594(13)	O(1)-Mo(1)-N(1)	90.55(6)
Mo(1)-N(3)	2.3886(13)	O(5)-Mo(1)-N(1)	129.25(6)
O(2)-O(3)	1.4807(16)	O(3)-Mo(1)-N(1)	132.97(5)
O(4)-O(5)	1.474(2)	O(4)-Mo(1)-N(1)	84.66(6)
		O(2)-Mo(1)-N(1)	88.72(5)
O(1)-Mo(1)-O(5)	104.25(6)	O(1)-Mo(1)-N(3)	172.30(5)
O(1)-Mo(1)-O(3)	102.04(6)	O(5)-Mo(1)-N(3)	82.77(5)
O(5)-Mo(1)-O(3)	91.52(6)	O(3)-Mo(1)-N(3)	80.68(5)
O(1)-Mo(1)-O(4)	103.24(6)	O(4)-Mo(1)-N(3)	79.37(5)
O(5)-Mo(1)-O(4)	44.90(6)	O(2)-Mo(1)-N(3)	76.24(5)

Table S3 Coordinates of computed compounds.

C_2H_4

C	0.000000	0.000000	0.665100
C	0.000000	0.000000	-0.665100
H	0.000000	0.923300	-1.238100
H	0.000000	0.923300	1.238100
H	0.000000	-0.923300	1.238100
H	0.000000	-0.923300	-1.238100

OC_2H_4

C	0.000000	0.734700	-0.371600
C	0.000000	-0.734700	-0.371600
H	0.920300	1.273500	-0.596400
H	-0.920300	-1.273500	-0.596400
H	-0.920300	1.273500	-0.596400
H	0.920300	-1.273500	-0.596400
O	0.000000	0.000000	0.855600

dmpz

H	-1.148700	1.973700	-0.000500
N	-0.620600	1.115500	-0.000200
N	0.733600	1.181200	0.000100
H	-3.076400	-0.047300	-0.874900
H	3.180300	0.480900	-0.000300
H	-3.069100	-0.076900	0.893800
C	-1.105400	-0.157400	-0.000600
C	-2.568500	-0.468900	0.000500
C	1.126900	-0.092900	0.000100
C	2.585800	-0.435300	0.000300
H	2.860000	-1.023800	0.883100
C	0.011800	-0.971600	-0.000500
H	-2.719800	-1.550200	-0.016900
H	2.859900	-1.024900	-0.881800
H	0.019700	-2.052100	-0.000800

$[Mo(O)(O_2)_2(dmpz)_2]$ (3)

Mo	-0.239500	-1.352900	-0.556400
O	-1.580400	-2.281900	-1.030900
O	1.050200	-2.620000	0.157800

O	0.222900	-2.054300	1.200100
O	0.731400	-1.133800	-2.247900
O	-0.138400	-0.005200	-2.017700
N	1.592700	0.300200	0.196200
N	1.773800	1.341100	-0.649200
H	1.171500	1.344000	-1.467600
C	2.857700	2.087800	-0.337400
C	3.397800	1.505000	0.799700
C	2.583600	0.388100	1.094800
H	4.272900	1.833600	1.341400
C	3.280400	3.275900	-1.142200
C	2.766700	-0.605900	2.201000
H	3.488900	3.004000	-2.183100
H	2.510800	4.056300	-1.150600
H	4.190400	3.708000	-0.720700
H	2.776500	-1.623200	1.803800
H	1.956400	-0.557000	2.934500
H	3.709200	-0.413900	2.720200
N	-1.555800	0.196900	0.357100
N	-2.267200	0.956800	-0.514800
H	-2.102000	0.827900	-1.506200
C	-3.108000	1.801400	0.120100
C	-2.925900	1.570000	1.477700
C	-1.952100	0.559000	1.588100
H	-3.432900	2.067800	2.290500
C	-4.022300	2.726100	-0.617900
C	-1.388400	-0.056600	2.828000
H	-0.338200	0.221800	2.954600
H	-1.432200	-1.147700	2.784100
H	-1.947600	0.286500	3.701000
H	-3.541900	3.136900	-1.511200
H	-4.935700	2.210600	-0.935300
H	-4.313900	3.559400	0.024500

TS_1

Mo	0.134000	-1.220800	-0.153900
O	-0.663400	-2.683400	-0.521500
O	1.905700	-1.791800	0.609700
O	0.490300	-1.299600	1.646300
O	1.061100	-0.870800	-1.866300
O	-0.192200	-0.176600	-1.872900

N	1.047800	1.211000	0.265400
N	0.932800	2.016800	-0.814400
H	0.477600	1.588700	-1.618900
C	1.527100	3.219300	-0.636400
C	2.050200	3.193000	0.647900
C	1.730600	1.918900	1.174700
H	2.594700	3.986500	1.139600
C	1.544500	4.277800	-1.694000
C	2.069900	1.365300	2.525400
H	2.022100	3.922000	-2.614000
H	0.532500	4.609100	-1.954000
H	2.101500	5.148900	-1.342500
H	1.796700	0.311300	2.580900
H	1.541200	1.909700	3.317400
H	3.141700	1.470500	2.726700
N	-1.832700	-0.234800	0.299400
N	-2.665600	-0.071600	-0.759300
H	-2.302200	-0.298900	-1.678300
C	-3.872800	0.403900	-0.384500
C	-3.810600	0.553300	0.994500
C	-2.521100	0.142000	1.388200
H	-4.598100	0.912400	1.640100
C	-4.971300	0.671400	-1.362800
C	-1.938600	0.122200	2.765300
H	-1.212400	0.931900	2.888300
H	-1.408800	-0.813300	2.956000
H	-2.731700	0.253000	3.505400
H	-4.673300	1.416900	-2.108100
H	-5.261600	-0.239100	-1.898200
H	-5.851200	1.050400	-0.839800
C	3.150600	-2.873300	-0.735500
C	3.610200	-1.619500	-0.461800
H	2.514700	-3.059700	-1.593600
H	3.418900	-3.722100	-0.116800
H	4.293900	-1.439100	0.360000
H	3.376100	-0.784600	-1.111100

A

Mo	-0.552300	-1.466800	-0.450500
O	-2.017300	-2.226300	-0.918100
O	-0.057400	-2.244400	1.013100

O	0.593200	-1.666400	-1.989500
N	1.602600	0.017600	0.408000
N	2.235100	0.642200	-0.610500
H	1.771200	0.557000	-1.513500
C	3.431900	1.160900	-0.247600
C	3.572200	0.870200	1.101900
C	2.409100	0.152500	1.467100
H	4.406800	1.133000	1.736100
C	4.329700	1.875000	-1.208500
C	2.041000	-0.401900	2.810200
H	4.595100	1.239400	-2.060800
H	3.861600	2.782900	-1.606800
H	5.255400	2.168500	-0.708800
H	1.414300	-1.288100	2.691900
H	1.490200	0.333300	3.410600
H	2.938700	-0.673900	3.373200
N	-1.522700	0.375200	0.164300
N	-1.638900	1.382000	-0.733200
H	-1.238300	1.239600	-1.653900
C	-2.317600	2.429800	-0.219400
C	-2.652100	2.071100	1.081200
C	-2.145800	0.774000	1.286300
H	-3.195900	2.672000	1.794300
C	-2.601400	3.666200	-1.009900
C	-2.258200	-0.103400	2.490700
H	-1.390200	-0.759900	2.583600
H	-3.147300	-0.740200	2.418400
H	-2.350600	0.503800	3.394300
H	-1.707300	4.022600	-1.531100
H	-3.379600	3.488300	-1.760300
H	-2.948100	4.461200	-0.347200
O	0.136000	-0.290000	-2.006900

B

H	-3.52217	2.63218	-2.59049
H	-2.31283	1.43351	-3.08961
C	-2.66205	2.04893	-2.25355
H	3.13171	.24169	-2.66402
H	-1.85161	2.72990	-1.98233
H	4.64075	.84557	-1.95228
O	.11861	-.11652	-1.82846

C	3.57658	.68339	-1.76586
H	-5.27015	1.12131	-1.03810
C	-3.03937	1.19018	-1.08798
H	3.09167	1.64780	-1.59599
C	-4.31855	.82013	-.62542
C	3.38569	-.21611	-.58568
H	5.35182	-1.20358	-.20769
N	-2.11604	.61385	-.30688
C	4.31145	-1.06876	.04927
MO	.13278	.52043	-.22680
N	2.20179	-.33118	.03072
C	-4.11572	-.01075	.47157
O	-.19079	2.44656	-.07904
N	-2.77772	-.10327	.62396
O	1.20118	2.14190	.02979
H	-4.90484	-1.78731	1.39944
C	3.62162	-1.70420	1.07652
N	2.35975	-1.22763	1.02569
H	-6.10286	-.53806	1.03352
O	-.21631	-.59676	1.11077
H	5.10239	-2.99144	1.90893
C	-5.08068	-.70634	1.37800
H	-2.17916	-.61725	1.27086
H	1.51309	-1.42535	1.55955
C	4.06438	-2.70780	2.09306
H	3.45368	-3.61631	2.05399
H	-5.00562	-.33537	2.40622
H	3.99973	-2.30550	3.11015

C

O	1.827300	1.161100	-1.131400
O	0.855600	-1.881800	-0.425600
O	2.273100	-1.707900	-0.199800
Mo	1.377900	-0.015700	0.043400
O	1.628400	0.560500	1.646700
H	-3.778700	1.493500	-0.066900
C	-2.899400	0.867700	-0.041300
C	-1.562700	1.297300	-0.076100
C	-2.872700	-0.522400	0.034400
N	-0.763700	0.213700	-0.029600
N	-1.571000	-0.872800	0.042300

H	-1.128300	-1.785700	0.082600
C	-1.009400	2.683900	-0.134600
H	-0.557600	2.959700	0.824700
H	-0.229500	2.761400	-0.897500
H	-1.804400	3.397500	-0.359200
C	-3.974100	-1.531700	0.073700
H	-3.762900	-2.327300	0.794600
H	-4.911400	-1.051700	0.360700
H	-4.118900	-1.996500	-0.907900

D

H	5.164300	0.341500	-3.448600
H	6.552000	-2.024100	-2.984000
H	3.347500	2.352400	-3.085800
C	4.641500	-0.033200	-2.581200
C	5.944300	-2.270100	-2.111300
H	5.483900	-3.248700	-2.285000
H	1.807400	1.644100	-2.544100
C	2.844200	1.847000	-2.258900
C	4.912900	-1.209600	-1.894700
H	6.613000	-2.362300	-1.248500
C	3.551500	0.572800	-1.925800
H	2.822800	2.517400	-1.394700
N	4.013600	-1.266000	-0.887300
N	3.186500	-0.194300	-0.887200
H	3.881500	-1.966800	-0.168900
O	-1.365500	1.263600	-2.063700
O	-2.603700	1.367700	-1.363100
O	0.518800	-0.195900	-1.078700
O	-1.918900	-1.547900	-0.961300
Mo	-1.435500	0.032000	-0.550400
Mo	1.435500	-0.032000	0.550400
O	1.918900	1.547900	0.961300
O	-0.518800	0.195900	1.078700
O	2.603700	-1.367700	1.363100
O	1.365500	-1.263600	2.063700
H	-3.881500	1.966800	0.168900
N	-4.013600	1.266000	0.887300
N	-3.186500	0.194300	0.887200
H	-6.613000	2.362300	1.248500
H	-2.822800	-2.517400	1.394700

H	-5.483900	3.248700	2.285000
C	-4.912900	1.209600	1.894700
C	-5.944300	2.270100	2.111300
C	-3.551500	-0.572800	1.925800
C	-2.844200	-1.847000	2.258900
H	-1.807400	-1.644100	2.544100
C	-4.641500	0.033200	2.581200
H	-6.552000	2.024100	2.984000
H	-3.347500	-2.352400	3.085800
H	-5.164300	-0.341500	3.448600

$[Mo_4O_{16}(dmpz)_6]$ (1)

Mo	0.221100	0.862000	1.275300
Mo	3.839200	-1.422800	1.661400
O	-0.341300	-0.917700	0.718400
O	1.407200	1.925500	2.444000
O	1.568300	2.312200	1.080400
O	-1.242300	1.689000	1.475300
O	2.380100	-0.464200	1.319000
O	4.488400	-2.835800	0.477400
O	5.276400	-1.654200	0.358000
O	4.277200	-1.544600	3.331300
N	0.063900	-0.138000	3.281200
N	1.160400	-0.316700	4.052000
H	2.056500	-0.007800	3.694400
N	2.423300	-3.128000	2.046500
N	1.114800	-3.072600	1.709300
H	0.701400	-2.205300	1.332900
N	4.904700	0.564600	1.667000
N	4.291900	1.700100	1.267800
H	3.294500	1.692200	1.027600
C	7.148800	-0.102100	2.520500
H	6.820300	-0.529200	3.472900
H	8.121600	0.372800	2.666100
H	7.258600	-0.925900	1.810100
C	0.882200	-1.007600	5.175200
C	2.651600	-4.365800	2.522400
C	1.452800	-5.097200	2.482700
H	1.308600	-6.121700	2.792600
C	0.490600	-4.241300	1.956400
C	6.158300	0.901400	2.018300

C	-0.962200	-0.714500	3.931500
C	-0.484700	-1.270200	5.132600
H	-1.064000	-1.797000	5.876200
C	3.999800	-4.815300	2.993200
H	4.736900	-4.734600	2.189300
H	3.951100	-5.855600	3.323000
H	4.350900	-4.198000	3.825200
C	4.664400	4.144200	0.986200
H	4.822300	4.334000	-0.081900
H	5.231500	4.892800	1.544400
H	3.601100	4.283400	1.199500
C	6.325400	2.285900	1.840900
H	7.218000	2.860700	2.038700
C	5.109500	2.767400	1.365500
C	-2.353500	-0.702300	3.382400
H	-2.735300	0.320300	3.304100
H	-3.019700	-1.275100	4.031300
H	-2.371200	-1.131100	2.376600
C	1.941900	-1.341500	6.175100
H	2.892200	-1.546400	5.672800
H	1.652800	-2.223100	6.751500
H	2.097500	-0.516000	6.879000
C	-0.965000	-4.440500	1.677800
H	-1.585600	-3.913600	2.411500
H	-1.211800	-5.503500	1.727800
H	-1.227600	-4.064400	0.684800
Mo	-0.221100	-0.862000	-1.275300
Mo	-3.839200	1.422800	-1.661400
O	0.341300	0.917700	-0.718400
O	-1.407200	-1.925500	-2.444000
O	-1.568300	-2.312200	-1.080400
O	1.242300	-1.689000	-1.475300
O	-2.380100	0.464200	-1.319000
O	-4.488400	2.835800	-0.477400
O	-5.276400	1.654200	-0.358000
O	-4.277200	1.544600	-3.331300
N	-0.063900	0.138000	-3.281200
N	-1.160400	0.316700	-4.052000
H	-2.056500	0.007800	-3.694400
N	-2.423300	3.128000	-2.046500
N	-1.114800	3.072600	-1.709300

H	-0.701400	2.205300	-1.332900
N	-4.904700	-0.564600	-1.667000
N	-4.291900	-1.700100	-1.267800
H	-3.294500	-1.692200	-1.027600
C	-7.148800	0.102100	-2.520500
H	-6.820300	0.529200	-3.472900
H	-8.121600	-0.372800	-2.666100
H	-7.258600	0.925900	-1.810100
C	-0.882200	1.007600	-5.175200
C	-2.651600	4.365800	-2.522400
C	-1.452800	5.097200	-2.482700
H	-1.308600	6.121700	-2.792600
C	-0.490600	4.241300	-1.956400
C	-6.158300	-0.901400	-2.018300
C	0.962200	0.714500	-3.931500
C	0.484700	1.270200	-5.132600
H	1.064000	1.797000	-5.876200
C	-3.999800	4.815300	-2.993200
H	-4.736900	4.734600	-2.189300
H	-3.951100	5.855600	-3.323000
H	-4.350900	4.198000	-3.825200
C	-4.664400	-4.144200	-0.986200
H	-4.822300	-4.334000	0.081900
H	-5.231500	-4.892800	-1.544400
H	-3.601100	-4.283400	-1.199500
C	-6.325400	-2.285900	-1.840900
H	-7.218000	-2.860700	-2.038700
C	-5.109500	-2.767400	-1.365500
C	2.353500	0.702300	-3.382400
H	2.735300	-0.320300	-3.304100
H	3.019700	1.275100	-4.031300
H	2.371200	1.131100	-2.376600
C	-1.941900	1.341500	-6.175100
H	-2.892200	1.546400	-5.672800
H	-1.652800	2.223100	-6.751500
H	-2.097500	0.516000	-6.879000
C	0.965000	4.440500	-1.677800
H	1.585600	3.913600	-2.411500
H	1.211800	5.503500	-1.727800
H	1.227600	4.064400	-0.684800

TS_2

H	4.649600	-2.267400	0.434100
N	1.448100	0.189000	0.050900
C	2.237900	1.274800	0.032700
H	1.822800	-1.803000	-0.105100
H	5.620500	-1.020100	-0.361200
N	2.257000	-0.886900	-0.096000
H	4.446900	1.495500	-0.164700
C	3.574500	0.860900	-0.119200
C	3.554300	-0.526900	-0.200600
C	4.653400	-1.525800	-0.371700
H	4.562500	-2.062700	-1.322300
C	1.679500	2.655600	0.159600
H	0.986900	2.863100	-0.661700
H	1.118900	2.762100	1.093400
H	2.485000	3.392500	0.144000
O	-0.917500	0.892800	1.584400
O	-0.135700	-1.876100	0.523700
Mo	-0.761400	-0.045600	0.165500
O	-0.748600	0.950400	-1.366300
O	-1.558200	-1.824600	0.338300
O	-2.418800	0.464000	-0.875000
C	-4.258200	0.384300	0.189200
C	-4.182200	-0.612000	-0.734200
H	-3.958800	0.226400	1.219800
H	-4.652600	1.361600	-0.064600
H	-3.832000	-1.603800	-0.472400
H	-4.532300	-0.463500	-1.749300

$[Mo(O)(O_2)_2(dmpz)]$

H	-4.108800	-2.256900	-0.442700
N	-0.907400	0.196700	-0.059000
C	-1.686700	1.290400	-0.144700
H	-1.309900	-1.783900	0.183300
H	-5.106400	-0.951100	0.214600
N	-1.734500	-0.864900	0.109100
H	-3.897400	1.537500	-0.063600
C	-3.030500	0.894800	-0.031300
C	-3.029500	-0.487000	0.131100
C	-4.147400	-1.463000	0.310200
H	-4.111200	-1.934100	1.298300

C	-1.115500	2.656900	-0.351800
H	-0.340300	2.873300	0.388200
H	-0.657500	2.738400	-1.343200
H	-1.902700	3.408900	-0.271700
O	1.615900	0.676000	-1.568900
O	0.670200	-1.935100	-0.413000
Mo	1.261400	-0.104000	-0.108200
O	1.243900	1.145300	1.366300
O	2.060900	-1.885600	-0.029800
O	2.534900	0.506800	1.238900

$[Mo(O)_2(O_2)(OC_2H_4)(dmpz)]$

H	-4.552400	-2.363000	-0.703800
N	-1.469600	0.200900	-0.050100
C	-2.311300	1.246300	-0.056000
H	-1.750500	-1.808700	0.040500
H	-5.593100	-1.214100	0.149300
N	-2.230900	-0.915500	0.033900
H	-4.536700	1.354600	0.017800
C	-3.633100	0.763600	0.011500
C	-3.548500	-0.621800	0.068100
C	-4.604600	-1.677000	0.148600
H	-4.508800	-2.271600	1.063600
C	-1.827700	2.659700	-0.100700
H	-1.403300	2.949100	0.867000
H	-1.039200	2.774800	-0.848000
H	-2.655700	3.333800	-0.331100
O	0.861900	1.321400	-1.162200
O	0.180900	-1.782800	-0.555100
Mo	0.734800	0.047600	-0.001000
O	0.708600	0.552000	1.649700
O	1.595800	-1.681200	-0.369800
O	3.070500	0.478600	0.230400
C	4.074400	-0.105200	-0.634700
C	4.012300	-0.469600	0.787700
H	3.678600	-0.799500	-1.370300
H	4.812900	0.612300	-0.982600
H	3.574600	-1.423900	1.066300
H	4.704300	-0.022200	1.496400