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# A Highly Efficient Dioxo($\mu$-oxo)molybdenum(VI) Dimer Catalyst for Olefin Epoxidation

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The oxo-bridged dimer $[Mo_2O_4(\mu_2\text{-}O)Cl_2(pzH)_4]$ (**1**; pzH = pyrazole) exhibits unusually high activity in the liquid-phase catalytic epoxidation of the cyclic olefins cyclooctene and (*R*)-(+)-limonene under mild conditions and in the absence of additional organic solvents, using *tert*-butyl hydroperoxide as the oxidant. The complex is stable under the reaction conditions and can be used in further catalytic runs without significant loss of performance. An X-ray crystallographic investigation reveals that **1** has an unprecedented and extremely rare all-cis configuration at each of the $MoO_2(\mu_2\text{-}O)Cl(pzH)_2$ cores, which can be understood by considering supramolecular contacts and geometric factors.

High-valent $d^0$ transition-metal complexes, such as $V^V$, $Mo^{VI}$, and $Re^{VII}$, are versatile catalysts for the epoxidation of alkenes.[1] In the late 1960s, molybdenum and tungsten complexes played an important role in homogeneous industrial catalysis in the Arco and Halcon processes, involving the production of propylene oxide using alkyl hydroperoxides as oxidants.[1a] Several oxomolybdenum(VI) complexes have recently been investigated as catalysts for liquid-phase olefin epoxidation, usually employing *tert*-butyl hydroperoxide (TBHP) as the mono-oxygen source.[2] Epoxides are important building blocks for the fine chemical and pharmaceutical industries. The present aim is to find highly active, selective, and stable catalysts that can be used under mild conditions and in the absence of environmentally unattractive solvents such as chlorinated hydrocarbons. So far, only the $(\eta^5\text{-}C_5R_5)MoO_2X$ complexes can match the highly active and well-characterized $Re^{VII}$ epoxidation catalyst methyltrioxorhenium (MTO).[3] Oxomolybdenum(VI) complexes containing bridging $\mu$-oxo groups (Mo−O−Mo) have been less studied as catalysts or catalyst precursors for olefin epoxidation,[4] despite the fact that binuclear oxo−metal entities have been shown to be key intermediates in many catalytic systems,[5] especially those concerning supported molybdenum oxides.[6] Here we describe the synthesis and characterization of a new dioxo($\mu$-oxo)molybdenum(VI) complex exhibiting unique structural features in the solid state and unusually high activity in the catalytic epoxidation of cyclic olefins.

Treatment of $MoO_2Cl_2$ with 2 equiv of pyrazole (pzH) monohydrate in tetrahydrofuran (THF) at room temperature produces quantitative $[Mo_2O_4(\mu_2\text{-}O)Cl_2(pzH)_4]$ (**1**) as an air- and moisture-sensitive pale-green solid with 90% yield.[7] The IR spectrum contains diagnostic bands centered at 933 and 913 $cm^{-1}$ for the symmetric and asymmetric stretching modes of the *cis*-dioxo unit and a band at 756 $cm^{-1}$ for the $\mu_2$-oxo

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(7) $MoO_2Cl_2$ (0.400 g, 2.0 mmol) was treated with pzH (0.136 g, 4.0 mmol) in THF at room temperature for 2 h. The solvent was then removed under vacuum and the solid product washed with diethyl ether and hexane, yielding compound **1** as a pale-green solid (0.56 g, 90%). Calcd for $C_{12}H_{16}Cl_2Mo_2N_8O_5$: C, 23.3; H, 2.6; N, 18.15. Found: C, 23.75; H, 3.0; N, 17.85. Selected $\nu_{max}/cm^{-1}$: 3330m [$\nu$(N−H)], 3141m [$\nu$(C−H)], 3000−2500br [$\nu$(N−H)], 1518s, 1482s, 1469s, 1402s, 1348s, 1270m, 1230w, 1163m, 1125s, 1072m, 1059s, 1046m, 933s [$\nu_{sym}$(Mo═O)], 913m [$\nu_{asym}$(Mo═O)], 896s, 875w, 780vs, 756vs [$\nu_{asym}$(Mo−O−Mo)], 611m, 555m, 383m, 335m [$\nu_{asym}$(Mo−Cl)]. $^1H$ NMR (300.13 MHz, 293 K, acetone-$d_6$, $Me_4Si$): $\delta$ 7.97 (8 H, br s, $H_{3,5}$), 6.60 (4 H, s, $H_4$). The magnetic equivalence of the pzH protons at positions 3 and 5 can be explained in terms of intermolecular exchange involving the pzH rings combined with intramolecular exchange or “shuttling” of the hydrogen and molybdenum between each of the four pairs of nitrogen atoms, which is common in pzH complexes. Upon cooling of the solution to 263 K, the two resonances broaden and collapse at 243 K. Below 213 K, the exchange processes are sufficiently slow to allow the observation of several well-separated signals for each of the protons (e.g., four $H_4$ signals are resolved in the 6.3−7.1 ppm range with integrals of 1 H each).

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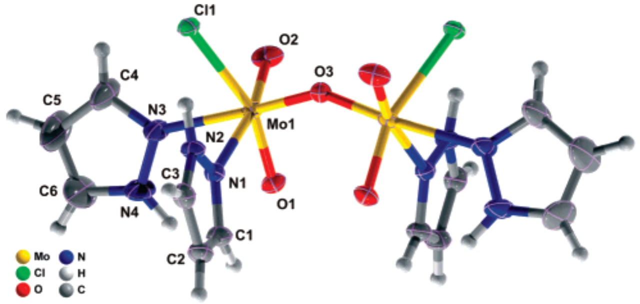
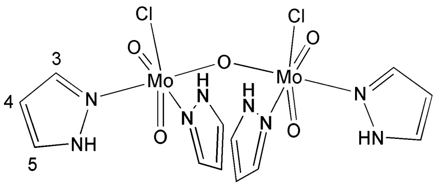


**Figure 1.** Molecular structure of the binuclear complex **1**, represented with thermal ellipsoids drawn at the 60% probability level and showing the labeling scheme for all non-hydrogen atoms composing the asymmetric unit. Selected bond lengths (Å) and angles (deg): Mo1−O1 1.7116(17), Mo1−O2 1.7066(18), Mo1−O3 1.8887(7), Mo1−N1 2.323(2), Mo1−N3 2.205(2), Mo1−Cl1 2.5189(7); O1−Mo1−O3 103.39(9), O1−Mo1−N1 83.20(8), O1−Mo1−N3 85.10(8), O1−Mo1−Cl1 159.38(6), O2−Mo1−O1 104.36(9), O2−Mo1−O3 101.73(9), O2−Mo1−N1 169.24(8), O2−Mo1−N3 91.14(9), O2−Mo1−Cl1 90.48(7), O3−Mo1−N1 83.60(7), O3−Mo1−N3 162.09(6), O3−Mo1−Cl1 87.14(6), N1−Mo1−Cl1 80.39(6), N3−Mo1−N1 81.77(8), N3−Mo1−Cl1 80.29(6).

bridge. Medium-intensity absorption bands at 3330 and 3141 cm$^{-1}$ are assigned to $\nu$(N−H) and $\nu$(C−H), and a broad $\nu$(N−H) band in the 2500−3000 cm$^{-1}$ region indicates strong hydrogen bonds in the solid state. A sharp medium-intensity band at 335 cm$^{-1}$ is assigned to $\nu_{asym}$(Mo−Cl). The presence of the $\nu$(N−H) absorptions is consistent with the coordination of the pzH ligands in the neutral monodentate form.



**1**

Figure 1 shows the molecular structure of **1** as determined by X-ray diffraction analysis, along with selected bond lengths and angles.[8] A single Mo$^{6+}$ center is coordinated to two pzH ligands, one chloride, two terminal oxo groups, and a $\mu_2$-bridging oxo group located on a crystallographic twofold axis. The $MoClN_2O_3$ octahedral coordination is highly distorted as a direct consequence of the very distinct chemical nature of the ligands. While the bond lengths range from 1.7066(18) Å (for one terminal oxo group) to 2.5189(7) Å (for the coordinated chloride anion), the cis and trans internal octahedral angles are in the 80.29(6)−104.36(9)° and 159.38(6)−169.24(8)° ranges. The central $\mu_2$-bridging oxo group imposes a Mo1···Mo1$^{i}$ separation of 3.6595(7) Å, with a Mo1−O3−Mo1$^{i}$ bridging angle of 151.30(14)°. This value is significantly smaller than the 171° reported for the complex $[Mo_2O_4(\mu_2\text{-}O)Cl_2(DMF)_4]$ (DMF = *N*,*N*-dimethylformamide),[9] which, to the best of our knowledge, is the only other closely related compound that has been structurally characterized. The DMF adduct adopts the common *cis*-oxo,*trans*-X,*cis*-L configuration at each of the metal centers (i.e., the chloride is trans with respect to the bridging oxo), while complex **1** has an unprecedented all-cis configuration (i.e., the chloride is cis with respect to the bridging oxo). Even for monomeric complexes of the type $MO_2X_2L_2$ (M = Mo, W), only a handful of examples have been structurally characterized that exhibit the all-cis geometry.[10] The general rule for mixed-ligand $MO_2X_2L_2$ species is that, when given a choice, the weaker donor atoms belonging to L are found to be trans to the terminal oxygen atoms, where they are not directly competing for the available empty metal d orbitals.[11]

The structural differences between the pzH and DMF complexes can be understood by considering supramolecular contacts and geometric factors. While in the DMF adduct intermolecular interactions seem to be limited to rather weak C−H···(Cl,N,O) contacts,[9] in **1** there is significant bonding between neighboring complexes via a series of N−H···(Cl,O) interactions (despite the presence of similar intramolecular interactions; see the Supporting Information for details). To reduce steric hindrance within the complex, the chloride anions in the DMF complex are located at apical positions. Although minimization of the steric hindrance related to the coordinated pzH ligands is met in **1** (symmetry-related moieties are structurally located in the furthest possible positions), this is not so for the chloride anions. Thus, the $\mu_2$-oxo bridge is bent so that the two Mo−Cl bonds point in opposite directions, ultimately positioning these anions in the furthest possible positions, while at the same time the strength of the N−H···Cl hydrogen-bonding interactions is reinforced. Close packing of individual binuclear complexes in **1** is further mediated by a variety of supramolecular contacts, including $\pi-\pi$ (involving the apical pzH moieties) and C−H···$\pi$ contacts, plus a number of weak C−H···(Cl,N,O) interactions.

The catalytic epoxidation of the cyclic olefins cyclooctene (Cy8) and limonene using 5.5 M TBHP in decane was carried out at 328 K in the presence of **1** and no additional solvent.[12] With cyclooctene as the substrate, 1,2-epoxycyclooctane was produced as the only product, with 90% yield, after 5 min, with a turnover frequency (TOF) of 1080 mol mol$_{cat}^{-1}$ h$^{-1}$ (molar ratio of **1**:Cy8:TBHP = 1:100:159; Figure 2). When the quantity of **1** was reduced by half, the TOF increased to 1800 mol mol$_{cat}^{-1}$ h$^{-1}$. The registered catalytic performance

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(8) Crystal data: $C_{12}H_{16}Cl_2Mo_2N_8O_5$, $M$ = 615.11, monoclinic, space group $C2/c$, $Z$ = 4, $a$ = 12.549(3) Å, $b$ = 11.284(2) Å, $c$ = 16.009(3) Å, $\gamma$ = 11.72(3)°, $V$ = 2106.0(9) Å$^3$, $\mu$(Mo Kα) = 1.486 mm$^{-1}$, $D_c$ = 1.940 g cm$^{-3}$, brown blocks with a crystal size of 0.12 × 0.12 × 0.10 mm$^3$. Of a total of 6074 reflections collected, 2402 were independent ($R_{int}$ = 0.0308). Final R1 = 0.0259 [$I > 2\sigma(I)$] and wR2 = 0.0616 (all data). Data completeness to $\theta$ = 27.49°, 99.3%. CCDC 639310.

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(12) The catalytic epoxidations were carried out at 328 K and atmospheric pressure in a reaction vessel equipped with a magnetic stirrer. The reactions were followed by gas chromatography (GC; Varian 3900, column DB-5, 30 m × 0.25 mm, or CyclosilB, 30 m × 0.25 mm) and GC−mass spectrometry (HP 5890 series II GC; HP 5970 series mass selective detector) using helium as the carrier gas. For the cyclooctene/TBHP system, complex **1** only partially dissolved, and after a catalytic run, the undissolved solid could be separated by centrifugation. Prior to reuse, the recovered solid was washed thoroughly with hexane and dried under reduced pressure.

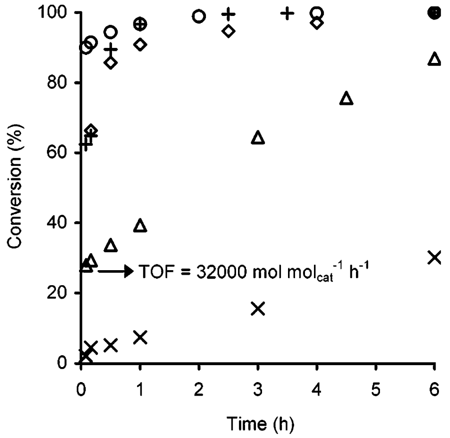

**Figure 2.** Kinetic profiles of olefin epoxidation in the presence of **1** at 328 K. Molar ratio catalyst:olefin:oxidant = 1:100:159: cyclooctene/TBHP (○, run 1; +, run 2); cyclooctene/$H_2O_2$ (×); limonene/TBHP (◇). Molar ratio catalyst:cyclooctene:TBHP = 0.0001:1:2 (Δ).

is superior to that reported for monomeric complexes of the type $MoO_2Cl_2L_2$ containing either monodentate or bidentate neutral N,S,O ligands ($L_2$). Indeed, under similar reaction conditions, the monomeric complexes typically exhibit initial activities in the range of 20−600 mol $mol_{cat}^{-1}$ $h^{-1}$,[13,14] with TOFs between 240 and 460 mol $mol_{cat}^{-1}$ $h^{-1}$ reported for complexes bearing monodentate or bidentate pzH or pyrazolylpyridine-type ligands.[14] The $MoO_2Cl_2L_2$ complexes are generally less active than those belonging to the ($\eta^5$-$C_5R_5$)$MoO_2Cl$ family in the catalysis of the same reaction. For ($\eta^5$-$C_5Bz_5$)$MoO_2Cl$ (Bz = benzyl) and a complex:Cy8:TBHP molar ratio of 0.0001:1:2, a TOF of 20000 mol $mol_{cat}^{-1}$ $h^{-1}$ was reported, which is greater than the highest TOFs previously recorded for the MTO/$H_2O_2$ catalytic epoxidation system.[3] Under similar reaction conditions, complex **1** gave a TOF of 32 000 mol $mol_{cat}^{-1}$ $h^{-1}$ and conversion increased linearly with time to reach 87% at 6 h, with a quantitative epoxide yield within 24 h. This contrasts with that observed for the known highly active ($\eta^5$-$C_5Bz_5$)$MoO_2Cl$ complex which suffers irreversible catalyst deactivation during the first catalytic run, ultimately resulting in a major decrease in the reaction rate after 1 h (cyclooctene conversion increased from 32% at 4 h to 48% at 24 h).

To assess the stability of **1** under the catalytic reaction conditions, two consecutive runs of 24 h were carried out at 328 K. Conversion at 1 h was 97% for the two runs (Figure 2). The IR spectrum of the recovered catalyst after the first run showed the characteristic $\nu$(N−H), $\nu$(C−H), $\nu$(Mo═O), and $\nu$(Mo−$O_b$) absorption bands, unchanged with respect to those exhibited by a fresh catalyst, along with new weak-intensity bands at 2863 and 2974 $cm^{-1}$, which indicate the presence of *tert*-butyl groups. From previous experimental and theoretical studies involving $MoO_2X_2L_2$ complexes, it is known that *tert*-butyl alcohol, a product of the decomposition of TBHP, can act as a competitive inhibitor for the attack of TBHP at the $Mo^{VI}$ center.[3,13] It is plausible to assume that, after the first catalytic run with **1**, a fraction of the recovered solid contained coordinated *tert*-butyl alcohol, thus accounting for the lower epoxidation rate observed in the first few minutes of the second catalytic run.

When 30% aqueous hydrogen peroxide was used as the oxidant instead of TBHP, with acetonitrile as a cosolvent, **1** was completely dissolved to give a homogeneous mixture. However, the reaction was slower, possibly because of the influence of coordinating water and acetonitrile moieties (Figure 2). Despite the slower reaction, the epoxide selectivity was 100% and the epoxide yield increased with time, reaching about 75% at 30 h. These results, coupled with the observation that the pale-yellow color of the reaction mixture did not change during the run, strongly suggest that **1** is a relatively robust epoxidation catalyst.

The outstanding catalytic performance of **1** extends to the epoxidation of (*R*)-(+)-limonene with TBHP to give limonene oxide. After 10 min, 67% limonene oxide was yielded as the only product (Figure 2). The reaction was complete within 6 h, giving limonene dioxide as a secondary product with 41% selectivity.

In conclusion, we show that **1** is one of the most active and selective catalysts for the liquid-phase epoxidation of cyclic olefins reported to date. Current work focuses on mechanistic studies and the characterization of the active intermediate species, as well as applying the complex in other catalytic organic transformations and preparing analogous complexes with pzH-derived ligands.

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**Supporting Information Available:** Crystallographic data for **1** in CIF format and schematic representations of hydrogen-bonding interactions and crystal packing. This material is available free of charge via the Internet at http://pubs.acs.org.

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