DOI: 10.1002/ejic.200601054

A Two-Dimensional, Hydrogen-Bond-Cross-Linked Molybdenum(VI) Network Polymer with Catalytic Activity

Yi Luan,[a] Ge Wang,*[b] Rudy L. Luck,[c] and Mu Yang[b]

Keywords: Hydrogen bonds / Crystal engineering / Hydrogen peroxide / Epoxidation / Molybdenum

The new hybrid inorganic–organic polymer $[MoO_2Cl_2(H_2O)_2]\cdot(H_2dipy\text{-}pra)Cl_2$ (**1**), where dipy-pra = 1,3-bis(4-pyridyl)propane, has been synthesized and crystallographically characterized. $MoO_2Cl_2(H_2O)_2$ and the $[H_2dipy\text{-}pra]^{2+}$ cation are cross-linked by Mo–H_2O···Cl and H_2dipy-pra···Cl hydrogen bonds to form a two-dimensional layer structure. Complex **1** is an efficient catalyst, with H_2O_2 as the oxygen-source oxidant and $NaHCO_3$ as the cocatalyst, in the epoxidation of olefinic compounds under ambient conditions.

The design and synthesis of metal–organic coordination polymers that is based on the strategy of crystal engineering is an emerging area, and a variety of novel supramolecular architectures have been obtained. Moreover, coordination polymers are used in areas such as magnetism,[1,2] optoelectronics,[3] guest exchangeability,[4,5] and catalysis.[6] The concept of crystal engineering was first introduced as an approach to more efficient topochemical reactions in the early 1960s.[7] However, the synthesis of coordination polymers following the principles of crystal engineering was not achieved until 1995.[8,9] Several recent reviews have described how coordination polymers ranging from one-dimensional to three dimensional can be attributed to the rapid development of crystal engineering research.[10,11] Molybdenum- and tungsten-based supramolecular networks have also been investigated.[12] Zubieta described a molybdenum-based network that employed protonated 4,4′-bipyridine as a ligand serving to buttress the inorganic layers.[13] In light of recent successes in the construction of potentially useful coordination polymers, we wanted to utilize a bidentate ligand and a dioxidomolybdenum(VI) center to yield this type of metal–organic hydrogen-bond network by crystal engineering.

Organomolybdenum reagents have been used in a variety of oxidation reactions such as epoxidation and the oxidation of alcohols and sulfides. In the past few years, dioxidomolybdenum(VI) halide complexes have been found to be efficient epoxidation catalysts.[14] We reported a series of dioxidomolybdenum(VI) halide complexes that catalyze the epoxidation of olefins with *tert*-butyl hydroperoxide (TBHP).[15,16] From both an economic and an environmental viewpoint, there is a definite need for catalytic oxidations employing hydrogen peroxide as the stoichiometric oxidant, because hydrogen peroxide is environmentally friendly, cheap, and readily available.[17] To the best of our knowledge, there is no report regarding efficient epoxidations with H_2O_2 by using dioxidomolybdenum(VI) halide complexes. In the present work, the synthesis, crystal structure, and characterization of $[MoO_2Cl_2(H_2O)_2]\cdot(H_2dipy\text{-}pra)Cl_2$ is reported, as well as the potential of this complex as an epoxidation catalyst with hydrogen peroxide as the oxidant.

The key to our approach was the utilization of aromatic amines such as 1,3-bis(4-pyridyl)propane. It is known that under more acidic reaction conditions protonation of the aromatic amine provides an aromatic ammonium cation. Thus, the aromatic ammonium cations of a linear bidentate ligand can serve as a structure-directing template by virtue of multipoint hydrogen bonding between the cation and the metal complex to form a new hydrogen-bond network structure. Compound **1** was synthesized by the reaction of $MoO_2Cl_2(H_2O)_2$ and protonated dipy-pra.[18] Single-crystal X-ray diffraction studies on the sample obtained from the reaction revealed its composition, $[MoO_2Cl_2(H_2O)_2]\cdot(H_2dipy\text{-}pra)Cl_2$, and an extended structure composed of the building units shown in Figure 1.

The supramolecular structure of complex **1** is shown in Figure 2. Each dipy-pra molecule is linked by H-bonds to a H_2O molecule of two uncharged $MoO_2Cl_2(H_2O)_2$ units through external chloride anions. The two-dimensional polymeric structure was formed by H-bonded linkages (O2W···Cl4 = 3.087, N2···Cl4 = 3.100, O1W···Cl4 = 3.059, O2W···Cl3 = 3.125, O1W···Cl3 = 3.047, N1···Cl3 = 3.038 Å). The Mo–O(oxido) and Mo–Cl distances, and the *cis*-MoO(oxido)$_2$ and *trans*-MoCl$_2$ angles, are comparable

---

[a] Beijing University of Chemical Technology,
Beijing 100029, P. R. China
[b] School of Materials Science and Engineering, University of Science and Technology Beijing,
Beijing 100083, P. R. China
E-mail: gewang@mater.ustb.edu.cn
[c] Department of Chemistry, Michigan Technological University,
Houghton, MI 49931, USA

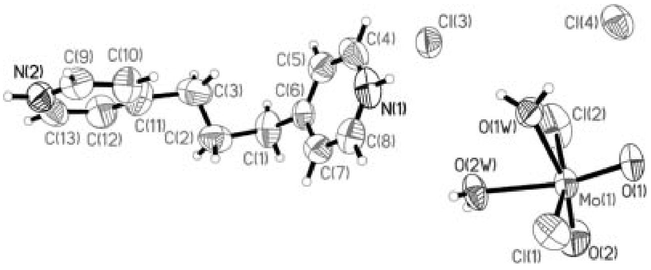


Figure 1. The building-block unit present in crystalline **1**. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å] and angles [°]: Mo(1)–O(2) 1.671(3), Mo(1)–O(1) 1.683(3), Mo(1)–O(1W) 2.217(3), Mo(1)–O(2W) 2.244(3), Mo(1)–Cl(1) 2.3739(13), Mo(1)–Cl(2) 2.3754(15), O(2)–Mo(1)–O(1) 105.12(16), O(1W)–Mo(1)–O(2W) 75.33(12), Cl(1)–Mo(1)–Cl(2) 162.13(6).

to those reported for other related $MoO_2Cl_2L_2$ complexes.[19] There are slight differences in the Mo–O(W) distances, and the shorter distance, i.e. Mo–O(1W) = 2.217(3) Å, correlates with a smaller O(1W)–Mo–O(2) angle of 164.07(14)° and the longer Mo–O(2W) distance of 2.244(3) Å with a larger O(2W)–Mo–O(1) angle of 166.08(14)°. This significant difference in Mo–O(W) bond lengths would appear to be related to the *trans* effect of the oxido ligand.

The catalytic property of compound **1** was then studied. With complex **1** as the catalyst, $NaHCO_3$ as the cocatalyst, and H_2O_2 as the oxygen source, we were able to catalyze the epoxidation of olefinic compounds. Cyclooctene was selected as a standard substrate for the optimization process with H_2O_2 in acetonitrile. A good yield (99%) of the epoxide was achieved with a catalytic amount of **1** (1 mol-%) and $NaHCO_3$ as cocatalyst (25 mol-%) after 1 h at room temperature (25 °C).

To evaluate the scope of this procedure, the oxidation of other alkenes was also studied (Table 1). As shown, carbocyclic alkenes were oxidized to produce the corresponding epoxy compounds in high yields (entries 1 and 2, Table 1). However, oxidation of the aromatic and linear alkenes required longer reaction times than that of the carbocyclic alkenes (entries 3 and 4, Table 1), especially 1-octene. Similarly, the allylic alcohols underwent oxidation without affecting the hydroxy group (entry 5, Table 1). Kuhn reported that dioxidomolybdenum derivatives are able to catalyze the olefin epoxidation reaction with TBHP but not with H_2O_2.[14]

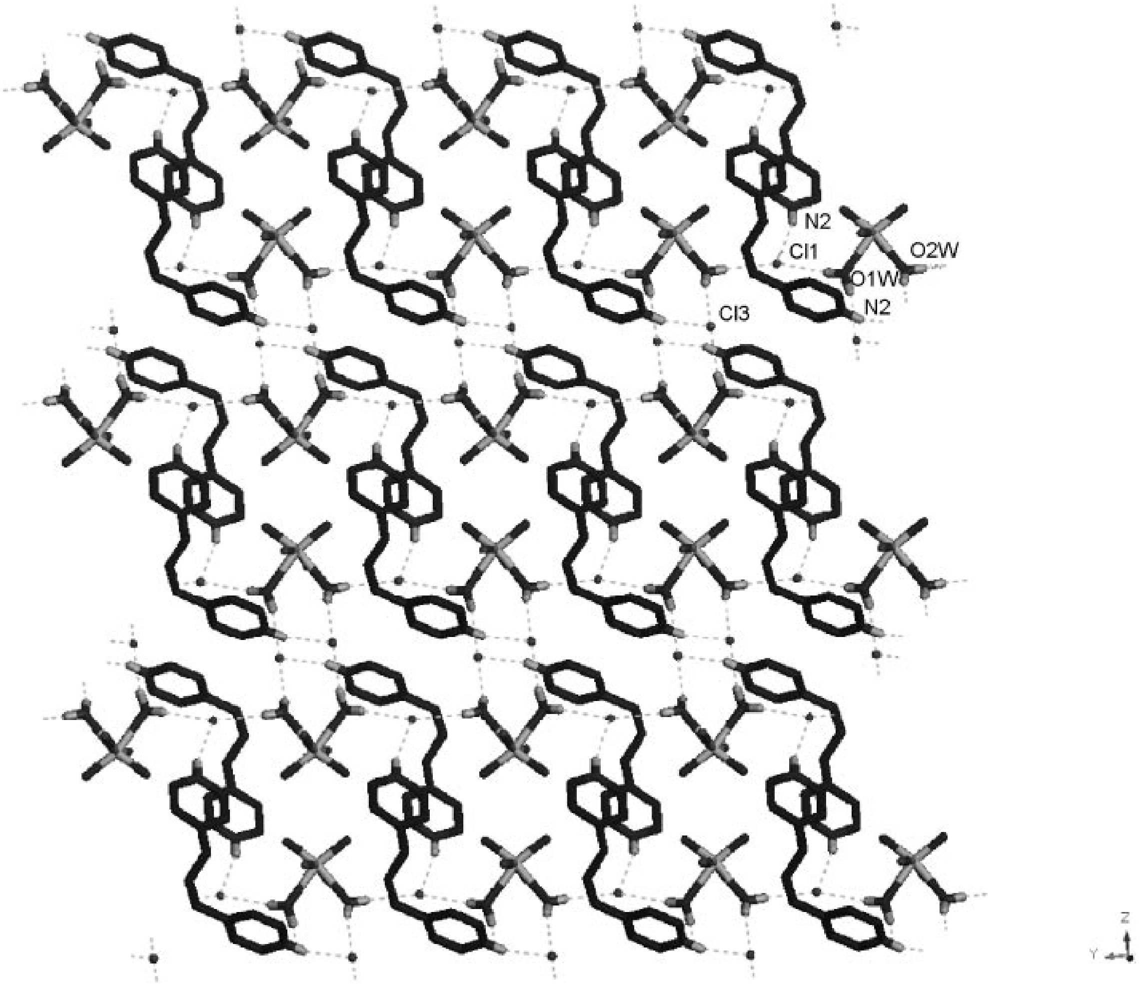
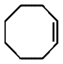
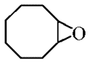
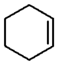
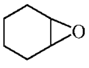
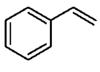
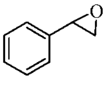
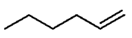
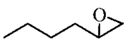
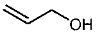
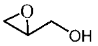


Figure 2. The two-dimensional layer structure of complex **1**. For clarity, part of the H atoms have been omitted.

Table 1. Epoxidation of selected olefins catalyzed by molybdenum(VI) complex **1**, with H_2O_2 as oxidant and hydrogencarbonate as cocatalyst.[a]

Entry	Substrate	Time [h]	Product	Yield[b] [%]	Selectivity [%]
1		1		99[c]	99
2		1.5		99[c]	99
3		4		86[c]	99
4		4		92	99
5		2		95	99

[a] Reaction conditions: the substrate (10 mmol), catalyst **1** (0.1 mmol, 1 mol-%), $NaHCO_3$ (2.5 mmol, 25 mol-%) and 30% aqueous H_2O_2 (40 mmol) dissolved in acetonitrile (10 mL) at 25 °C. [b] Determined by GC by using an internal standard technique. [c] Isolated yield.

Notably, the chemoselectivity was reduced at higher temperatures. In the epoxidation of cyclic alkenes (such as cyclohexene) at 50 °C, 2,3-epoxycyclohexanone and 2-cyclohexen-1-one were obtained in addition to the desired epoxide product. When the reaction was carried out at reflux temperature, i.e. 75 °C, the efficiency was significantly reduced. To confirm whether this reduction in efficiency was due to the conversion of $NaHCO_3$ (which acts as a cocatalyst) into Na_2CO_3, $NaHCO_3$ was replaced by Na_2CO_3; this resulted in almost no oxidation products, even after 24 h.[20]

Besides our system, Burgess and Bhattacharyya demonstrated that $MnSO_4$ and $[MoO(O_2)_2(saloxH)]$ can catalyze epoxidation reactions efficiently with $NaHCO_3/H_2O_2$.[21,22] The epoxidation of alkenes in the presence of hydrogencarbonate alone was also investigated.[20,23] Interestingly, the use of complex **1** or hydrogencarbonate alone gave much lower yields of epoxides than when they were used together.[21,22] Richardson showed that a key aspect of such reactions is that hydrogen peroxide and hydrogencarbonate combine in an equilibrium process to produce peroxymonocarbonate, HCO_4^-.[24,25] HCO_4^- may be more reactive than hydrogen peroxide and can be expected to attack the metal center or other more potent, activated groups at a much faster rate.[21] The mechanism for our epoxidation reaction is under investigation.

In conclusion, a novel 2D network material with the general formula $[MoO_2Cl_2(H_2O)_2]\cdot(dipy\text{-}praH_2)Cl_2$ has been synthesized and successfully applied to epoxidation reactions. Our current observations suggest that, under acidic conditions, the protonated $[H_2dipy\text{-}pra]^{2+}$ cation serves as a structure-directing template by using multipoint hydrogen bonding in the formation of infinite frameworks. The epoxidation of alkenes was studied with hydrogen peroxide in the presence of complex **1** to give products in high yields. This reaction provides a new environmentally friendly route for the conversion of a variety of alkenes to their respective epoxides.

Acknowledgments

We thank the NSFC (Grant no. 2220406003) and the Program for New Century Excellent Talents in University (NCET-05–0103) for support. We also thank Dr. Zhan Shi at Jilin University for the determination of the X-ray structure.

---

[1] X. Y. Wang, B. L. Li, X. Zhu, S. Gao, *Eur. J. Inorg. Chem.* **2005**, *16*, 3277–3286.

[2] K. Inoue, T. Hayamizu, H. Iwamura, D. Hashizume, Y. Ohashi, *J. Am. Chem. Soc.* **1996**, *118*, 1803–1804.

[3] O. R. Evans, W. B. Lin, *Chem. Mater.* **2001**, *13*, 2705–2712.

[4] O. M. Yaghi, C. E. Davis, G. M. Li, H. L. Li, *J. Am. Chem. Soc.* **1997**, *119*, 2861–2868.

[5] S. Kawata, S. Kitagawa, H. Kumagai, C. Kudo, H. Kamesaki, T. Ishiyama, R. Suzuki, M. Kondo, M. Katada, *Inorg. Chem.* **1996**, *35*, 4449–4461.

[6] K. Endo, T. Kake, T. Sawaki, O. Hayashida, H. Masuda, H. Aoyama, *J. Am. Chem. Soc.* **1997**, *119*, 4117–4122.

[7] B. F. Hoskins, R. Robson, *J. Am. Chem. Soc.* **1990**, *112*, 1546–1554.

[8] S. Mann, *J. Chem. Soc., Dalton Trans.* **1993**, 1–9.

[9] L. R. MacGillivray, S. Subramanian, M. J. Zaworotko, *J. Chem. Soc., Chem. Commun.* **1994**, 1325–1326.

[10] K. Biradha, M. Sarkar, L. Rajput, *Chem. Commun.* **2006**, 4169–4179.

[11] N. W. Ockwig, O. Delgado-Friedrichs, M. O'Keeffe, O. M. Yaghi, *Acc. Chem. Res.* **2005**, *38*, 176–182.

[12] B. Sieklucka, R. Podgajny, T. Korzeniak, P. Przychodzen, R. Kania, *Cr. Chim.* **2002**, *5*, 639–649.

[13] P. J. Zapf, R. C. Haushalter, J. Zubieta, *Chem. Commun.* **1997**, 321–322.

[14] F. E. Kuhn, A. M. Santos, A. D. Lopes, I. S. Goncalves, E. Herdtweck, C. C. Ramao, *J. Mol. Catal. A* **2000**, *164*, 25–38.

[15] G. Wang, G. Chen, R. L. Luck, Z. Q. Wang, Z. C. Mu, D. G. Evans, X. Duan, *Inorg. Chim. Acta* **2004**, *357*, 3223–3229.

[16] G. Wang, L. S. Feng, R. L. Luck, D. G. Evans, Z. Q. Wang, X. Duan, *J. Mol. Catal. A* **2005**, *241*, 8–14.

[17] R. Noyori, M. Aoki, K. Sato, *Chem. Commun.* **2003**, 1977–1986.

[18] Experimental details: MoO_3 (0.826 g, 5.74 mmol) was dissolved in excess concentrated HCl by stirring at 40 °C for 4 h; a pale yellow solution was obtained. The solution was cooled in an ice bath, and a solution of a dipy-pra (1.138 g, 5.74 mmol) in ethanol (10 mL) was then added in portions. After stirring for 6 h, a yellow solution was obtained, which when left overnight at ca. 4 °C afforded the lemon yellow crystalline complex **1** in 1.48 g, 51% yield. The characterization results are as follows: $C_{13}H_{20}Cl_4MoN_2O_4$ (506.66): calcd. C 30.85, H 3.98, Mo 18.96, N 5.54, O_2^{2-} 12.65; found C 30.71, H 4.11, Mo 18.91, N 5.46, O_2^{2-} 12.87. IR (KBr disc; selected bands): 952, 936 (MoO_2, asym.), 906 (MoO_2, sym.) cm^{-1}. Crystal data for **1** at 293 K: $C_{13}H_{20}N_2O_4Cl_4Mo$, M = 506.05, triclinic, space group $P\bar{1}$, yellow plate crystal (0.32 mm × 0.28 mm × 0.24 mm), a = 8.6398(17), b = 8.6481(17), c = 13.944(3) Å, α = 85.33(3), β = 83.03(3), γ = 82.44(3)°, V = 1022.9(4) $Å^3$, Z = 2, $D_{calcd.}$ = 1.643 Mg/m^3, μ = 1.182 mm^{-1}, $F(000)$= 508, 10144 reflections measured, 4632 unique. CCDC-614792 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[19] M. J. Taylor, J. R. Wang, C. E. F. Rickard, *Polyhedron* **1993**, *12*, 1433–1435.

[20] H. R. Yao, D. E. Richardson, *J. Am. Chem. Soc.* **2000**, *122*, 3220–3221.
[21] B. S. Lane, M. Vogt, V. J. DeRose, K. Burgess, *J. Am. Chem. Soc.* **2002**, *124*, 11946–11954.
[22] S. K. Maiti, S. Dinda, N. Gharah, R. Bhattacharyya, *New J. Chem.* **2006**, *30*, 479–489.
[23] W. C. Frank, *Tetrahedron: Asymmetry* **1998**, *9*, 3745–3749.
[24] J. Flanagan, D. P. Jones, W. P. Griffith, A. C. Skapski, A. P. West, *J. Chem. Soc., Chem. Commun.* **1986**, 20–21.
[25] A. Adam, M. Mehta, *Angew. Chem. Int. Ed.* **1998**, *37*, 1387–1388.

Received: November 10, 2006