

## Hydrogen-bond-supported 3D Networks: Two Different Polymeric Structures Featuring Chlorine Atoms as Ligands and as Anions and Investigations as Epoxide Catalysts

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Two novel hydrogen-bonded network polymers,  $[\text{MoO}_2\text{Cl}_2(\text{H}_2\text{O})_2][4,4'\text{-H}_2\text{bipy}]^{2+} \cdot 2\text{Cl}^-$  (**1**) and  $[\text{MoO}_2\text{Cl}_4]^{2-}[4,4'\text{-H}_2\text{-bipy}]^{2+}$  (**2**) [bipy = bipyridine] contained different three-dimensional NH...Cl hydrogen-bonded arrangements resulting in different polymeric structures; complex **1** or **2** as catalytic precursor,  $\text{H}_2\text{O}_2$  as a source of oxygen and  $\text{NaHCO}_3$  as cocatalyst showed great efficiency for the epoxidation of olefinic compounds under ambient conditions.

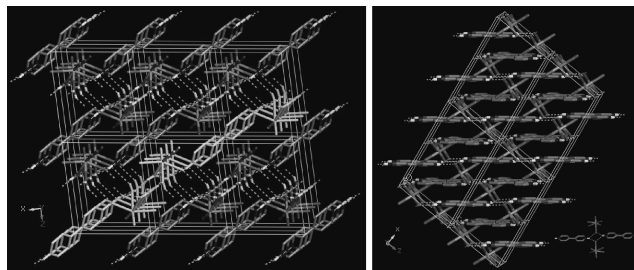
Organometallic crystal engineering of two- and three-dimensional organic-inorganic hybrid polymers has recently attracted significant attention, owing to the synthesis of a large number of novel supramolecular architectures with a wide variety of physical and chemical properties.<sup>1</sup> Recently, new synthetic strategies<sup>2</sup> utilizing different kinds of hydrogen bonds, such as NH...Cl interactions, have been reported.<sup>3</sup> Two main approaches for network structures have been employed: (i) anion-directed assembly connected network via NH...Cl<sup>-</sup> hydrogen bonds,<sup>4</sup> and (ii) metal-assisted, self-assembly processes to form a NH...ClMCl<sub>n-1</sub> hydrogen-bond network.<sup>5</sup> Slight modifications in the syntheses, such as changing the counter ions varying the structural characteristics of the polydentate organic ligand and in the metal-ligand ratios, result in supramolecular conformational isomerization. Based upon the strategy outlined as (i) above, the complex **1** has been synthesized. In contrast strategy (ii) allows for the formation of another dioxo-Mo<sup>VI</sup> polymeric complex **2** using different metal-ligand ratios.<sup>15</sup>

Dioxo-Mo<sup>VI</sup> complexes have been utilized as catalysts for a variety of oxidation reactions such as epoxidation and the oxidation of alcohols and sulfides.<sup>6</sup> Our interest in dioxo-Mo<sup>VI</sup> hydrogen-bond networks stems from previous studies on dioxomolybdenum(VI) complexes, that were demonstrated to be efficient epoxidation catalysts with *tert*-butyl hydroperoxide (TBHP) as the oxidant.<sup>7</sup> From both the economic and environmental viewpoints, employing  $\text{H}_2\text{O}_2$  as the stoichiometric oxidant is preferable to use of organic oxidants such as TBHP and PhIO for catalytic oxidations,<sup>8</sup> because the by-product  $\text{H}_2\text{O}$  is environmentally friendly and  $\text{H}_2\text{O}_2$  is cheap and readily available.<sup>9</sup> The two dioxo-Mo<sup>VI</sup> network polymers were obtained by crystal engineering design experiments, and their potential as catalytic precursors for epoxidation using  $\text{H}_2\text{O}_2$  as the oxidant have been investigated.

Despite the involvement of the  $[4,4'\text{-H}_2\text{bipy}]^{2+}$  cation in both hydrogen-bonding networks, **1** and **2** have completely different extended supramolecular structures. Complex **1** consists of the uncharged molybdenum complex  $[\text{MoO}_2\text{Cl}_2(\text{H}_2\text{O})_2]$  accompanied by the diprotonated bipyridinium molecule and two chloride anions. The Mo atom has a distorted octahedral coordination with cis-oxo groups, cis- $\text{H}_2\text{O}$  ligands and trans-







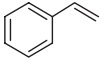
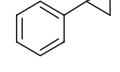


chlorine atoms. The Mo-O(oxo) and Mo-Cl distances, 1.668(3) and 1.680(3), and the cis-MoO(oxo)<sub>2</sub> and trans-MoCl<sub>2</sub> angles 103.60(18) and 156.44(4), are comparable to those reported for other related  $\text{MoO}_2\text{Cl}_2\text{L}_2$  complexes. The 3D hydrogen-bonded framework of compound **1** consists of interactions between  $[\text{MoO}_2\text{Cl}_2(\text{H}_2\text{O})_2]$ ,  $[4,4'\text{-H}_2\text{bipy}]^{2+}$ , and  $\text{Cl}^-$  (Figure 1 left). Each  $\text{Cl}^-$  counter ion is stabilized by strong hydrogen bonds with one  $[4,4'\text{-H}_2\text{bipy}]^{2+}$  and three other adjacent  $\text{MoO}_2\text{Cl}_2(\text{H}_2\text{O})_2$  centers resulting overall in a 2D network undulating sheet pattern. Adjacent layers of  $[4,4'\text{-H}_2\text{bipy}]^{2+}$  cations are arranged in a herringbone pattern when viewed perpendicular to the plane. The Cl...N and Cl...O distances (N(1)-H(1)...Cl(3) 3.123(3) Å, O(3)-H(3A)...Cl(3) 3.080(3) Å, O(4)-H(4B)...Cl(3) 3.080(3) Å, O(3)-H(3B)...Cl(3) 3.068(3) Å) are within the accepted range (2.91–3.53 Å), and the hydrogen bonds do not deviate much from linearity (162.2, 166(6), 175(7), and 167(6)°, respectively).

Interestingly enough in the structure of  $[\text{MoO}_2\text{Cl}_4]^{2-}[4,4'\text{-H}_2\text{bipy}]^{2+}$  (**2**), which consists of the biprotonated bipyridinium molecule and the molybdenum complex  $[\text{MoO}_2\text{Cl}_4]^{2-}$ , the Mo atom has a distorted octahedral geometry with cis-oxo groups and four chlorine atoms. The 4,4'- $\text{H}_2\text{bipy}$  molecules form linear chains in parallel layers connected to one another by N-H...Cl bonded interactions to two opposite  $[\text{MoO}_2\text{Cl}_4]^{2-}$  anions resulting in the 3D framework (Figure 1 right). Therefore,  $[\text{MoO}_2\text{Cl}_4]^{2-}[4,4'\text{-H}_2\text{bipy}]^{2+}$  (**2**) contains only N-H...Cl interactions as its structure-determining factor instead of the two kinds of interaction mentioned for **1**. The Cl...N distances in **2** are longer than those in compound **1**, N(1)-H(1)...Cl(1) 3.235(2), N(1)-H(1)...Cl(1) 3.227(2), and the angle of hydrogen bonds is different and deviates from linearity (141.1 and 128.2°, respectively), suggesting perhaps a more electrostatic nature to the bonding. It is noteworthy that in complex **2**, O atoms, bonded to Mo atoms located intra to the planes generated by the  $[4,4'\text{-H}_2\text{bipy}]^{2+}$  cations, situated at distances of 2.787 Å are closer than the sum of their van der Waals radii and perhaps suggestive of H bonds. This would imply that an OH or OH<sub>2</sub> formulation



**Figure 1.** Structure of the NH...Cl hydrogen-bonded layer in crystalline **1** and **2**.

**Table 1.** Complexes (**1**)-catalyzed epoxidation of selected olefins using H<sub>2</sub>O<sub>2</sub> as oxidant, bicarbonate as cocatalyst<sup>a</sup>

Entry	Substrate	Time/h	Product	Yield <sup>b</sup> /%		Selectivity/%
				1	2	
1		1		99	99	99
2		1.5		96	96	99
3		1		92	93	99
4		4		86	87	99
5		4		90	89	99

<sup>a</sup>Reaction conditions: a given substrate (10 mmol), catalyst **1** (0.1 mmol, 1 mol %), NaHCO<sub>3</sub> (2.5 mmol, 25 mol %) and 30% aqueous H<sub>2</sub>O<sub>2</sub> (40 mmol) were dissolved in acetonitrile (10 mL) at 25 °C. <sup>b</sup>Determined by GC using an internal standard technique.

would be required. The Mo=O distances at 1.680(3) Å argues strongly against such assignments.

The process by which the two complexes formed was different. The polymer **1**, which was composed of the neutral MoO<sub>2</sub>Cl<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub> molecule and the bipyridinium cation, employed chloride anions to attain neutrality and to direct the 3D polymerization. In contrast in polymer **2** the protonated ring nitrogen -NH<sup>+</sup> and [MoO<sub>2</sub>Cl<sub>4</sub>]<sup>2-</sup> were used as hydrogen-bond donors and acceptors, respectively. [MoO<sub>2</sub>Cl<sub>4</sub>]<sup>2-</sup> was presumably obtained from MoO<sub>2</sub>Cl<sub>2</sub> when more bipyridinium cation is generated by the addition of more 4,4'-bipy ligand to the reaction.

The catalytic epoxidation properties of compounds **1** and **2** were then assessed. We found that with complex **1** or **2** as catalytic precursor, NaHCO<sub>3</sub> as a cocatalyst, and H<sub>2</sub>O<sub>2</sub> as an 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<sub>2</sub>O<sub>2</sub> in acetonitrile. A good yield (99%) of the epoxide was achieved using a catalytic amount of **1** (1 mol %) and NaHCO<sub>3</sub> as cocatalyst (25 mol %) for 1 h at room temperature (25 °C) (Table 1, Entry 1). To evaluate the scope of this procedure, the oxidation of other alkenes was also studied (Table 1). The catalytic attributes of complex **2** were almost identical to those for complex **1** under similar conditions.

Dioxo-Mo<sup>VI</sup> complexes have been explored for and demonstrated the potential to be epoxidation catalysts. Kuhn et al. have reported that dioxo-Mo<sup>VI</sup> derivatives are able to catalyze the olefin epoxidation reaction with TBHP but not with H<sub>2</sub>O<sub>2</sub>.<sup>10</sup> In this catalytic system, dioxo-Mo<sup>VI</sup> complexes **1** and **2** were successfully applied as epoxidation catalysts using H<sub>2</sub>O<sub>2</sub> as the oxidant, NaHCO<sub>3</sub> as the cocatalyst. The epoxidation of alkenes in the presence of bicarbonate is known.<sup>11</sup> Interestingly in our system, the use of the dioxo Mo<sup>VI</sup> complexes **1** and **2** or bicarbonate alone gave much lower yields of epoxides (less than 10% or 30%, respectively) than when they were applied together.

The high yields (as listed in Table 1) were only obtained when catalyst and bicarbonate were applied in concert.

Dioxo-Mo<sup>VI</sup> complexes convert to oxodiperoxo-Mo<sup>VI</sup> in the presence of hydrogen peroxide.<sup>12</sup> Under our reaction conditions, it was assumed that the 4,4'-bipy ligand would coordinate to the resulting MoO(O<sub>2</sub>)<sub>2</sub> centers under alkaline conditions. This reassembled LMoO(O<sub>2</sub>)<sub>2</sub> complex could then act as catalyst with NaHCO<sub>3</sub> as the cocatalyst using H<sub>2</sub>O<sub>2</sub> as the oxygen source.<sup>13</sup> Bhattacharyya et al. have previously demonstrated that MnSO<sub>4</sub> and [MoO(O<sub>2</sub>)<sub>2</sub>(saloxH)] are efficient catalysts for epoxidation reactions in the presence of NaHCO<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>.<sup>14</sup> Yao and Richardson have shown that a key aspect of these reactions is that hydrogen peroxide and bicarbonate combine to produce peroxydicarbonate, HCO<sub>4</sub><sup>-</sup>.<sup>11</sup> HCO<sub>4</sub><sup>-</sup> would 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.

In summary, we have synthesized the first structurally distinct 3D hydrogen-bond networks **1** and **2** which consists of the dioxo-Mo<sup>VI</sup> and 4,4'-bipyridinium cation. We demonstrate that in the construction of a hydrogen-bonded network, complexes based on two different types of NH...Cl interactions can be obtained under slightly different conditions. The epoxidation of alkenes has also been examined in the presence of hydrogen peroxide and NaHCO<sub>3</sub> using complex **1** or **2**. This reaction provides an environmentally constructive route for the conversion of a variety of alkenes to their respective epoxides.

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