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A dinuclear oxomolybdenum(VI) complex, $[Mo_2O_6$(4,4′-di-*tert*-butyl-2,2′-bipyridine$)_2]$, displaying the $\{MoO_2(\mu\text{-}O)_2MoO_2\}^0$ core, and its use as a catalyst in olefin epoxidation

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ABSTRACT

The dinuclear complex $[Mo_2O_6$(di-*t*Bu-bipy$)_2]$ (**1**) (di-*t*Bu-bipy = 4,4′-di-*tert*-butyl-2,2′-bipyridine) was obtained as a minor product of the hydrothermal reaction of MoO_3 and di-*t*Bu-bipy, and structurally characterized by single-crystal X-ray diffraction. In the molecular structure of **1** two distorted MoO_6 octahedra share a common edge to form a dioxo-bridged Mo_2O_6 unit which is coordinated by di-*t*Bu-bipy ligands. The catalytic performance of **1** for the epoxidation of non-functionalized olefins using *tert*-butylhydroperoxide as oxidant compares favorably with that reported for other oxomolybdenum(VI) complexes bearing the same organic ligand. The catalyst exhibits regioselectivity toward internal olefin epoxidation over external olefin epoxidation.

The interest in complexes containing the *cis*-dioxomolybdenum(VI) unit stems from their use as catalysts for organic transformations, most notably the Oxirane process for the epoxidation of propylene [1], and as models for the active sites of oxo-transfer molybdoenzymes [2]. Mononuclear complexes of the type $[MoO_2X_mL_n]$ (X = mono/dianionic ligand, L = neutral ligand) [3] and the related mono-oxo-bridged dinuclear species $[(MoO_2X_mL_n)_2O]$ [4] have been shown to be active catalysts or catalyst precursors for the epoxidation of non-functionalized olefins, usually employing *tert*-butylhydroperoxide (TBHP) as the oxidant. Whereas the $\{MoO_2(\mu\text{-}O)MoO_2\}^{2+}$ core structure is quite common in oxomolybdenum(VI) chemistry, only a handful of dinuclear complexes displaying the dioxo-bridged unit $\{MoO_2(\mu\text{-}O)_2MoO_2\}^0$ have been reported and crystallographically characterized [5]. On the other hand, several reports serve to illustrate the potential importance of this core structure in homogeneous and immobilized molecular catalysts [6]. It is therefore desirable to synthesize new examples of these dinuclear complexes and examine their behavior as catalysts. In this communication we describe the synthesis, crystal and molecular structure of the complex $[Mo_2O_6$(di-*t*Bu-bipy$)_2]$ (di-*t*Bu-bipy = 4,4′-di-*tert*-butyl-2,2′-bipyridine), and a preliminary study of its performance as a catalyst for the epoxidation of non-functionalized olefins.

As part of our ongoing studies on the preparation and catalytic applications of molybdenum oxide/organoamine compounds, we recently found that the octanuclear complex $[Mo_8O_{22}(OH)_4$(di-*t*Bu-bipy$)_4]$ precipitates from the hydrothermal reaction of MoO_3 and di-*t*Bu-bipy in water in the mole ratio 1:1:580 at 160 °C for 3 d. The structure, chemistry and catalytic performance of this complex will be described in a separate publication [7]. When the filtered solution from this reaction is evaporated to dryness, the dinuclear complex $[Mo_2O_6$(di-*t*Bu-bipy$)_2]$ (**1**) is reproducibly obtained as a microcrystalline powder; single crystals (irregular colorless blocks) were obtained by slow evaporation of the filtered solution at room temperature [8]. The infrared spectrum of **1** is characterized by medium to very strong bands in the 850 to 950 cm^{-1} range assigned to ν(Mo=O), a very strong ligand band at 844 cm^{-1}, and a very strong band at 777 cm^{-1} associated with the Mo_2O_2 bridge [4b–4f,5b,5c]. Several ligand modes are observed in the 1000 to 1700 cm^{-1} range; the presence of the pyridyl ring stretching vibration at 1611 cm^{-1} is indicative of the bidentate coordination mode of the di-*t*Bu-bipy ligands to the Mo^{VI} centers [4e,9].

The single crystal X-ray structural analysis [10] revealed that **1** crystallizes in the monoclinic space group $P2_1/n$ with an asymmetric unit comprising a whole molecular unit of $[Mo_2O_6$(di-*t*Bu-bipy$)_2]$ (Fig. 1) and two water molecules of crystallization strongly hydrogen bonded to the hybrid complexes (see below for additional structural details) [15]. The crystallographically independent dinuclear neutral complex is approximately centrosymmetric but the overall crystal symmetry does not reflect this local feature. This occurs because of

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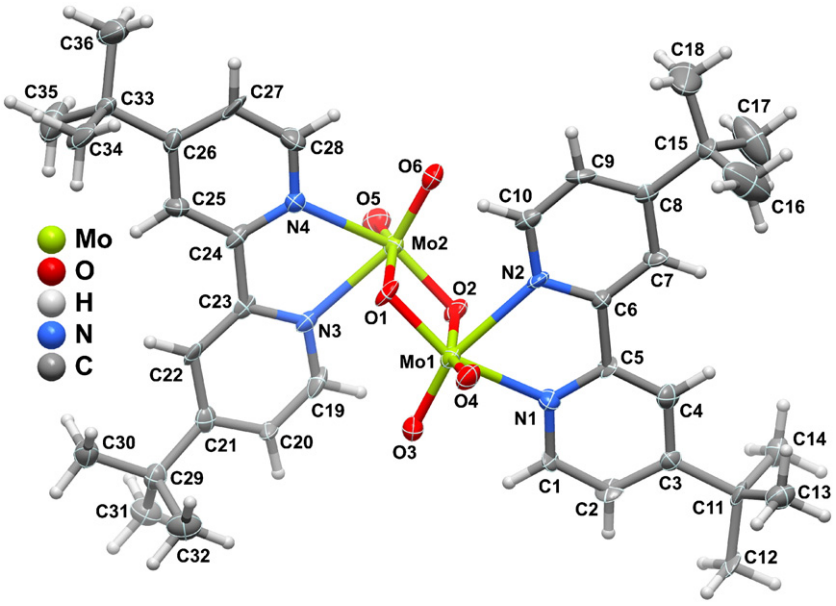

Fig. 1. Molecular structure of **1** with thermal ellipsoids drawn at the 70% probability level. Hydrogen atoms are represented as small spheres with arbitrary radii. Selected bond lengths (Å): Mo1 – O1 1.805(4), Mo1 – O2 2.217(5), Mo1 – O3 1.707(4), Mo1 – O4 1.714(5), Mo2 – O1 2.198(4), Mo2 – O2 1.798(4), Mo2 – O5 1.720(5), Mo2 – O6 1.716(5), Mo1 – N1 2.277(5), Mo1 – N2 2.339(5), Mo2 – N3 2.311(5), Mo2 – N4 2.270(5). Selected bond angles (°): O1 – Mo1 – O2 77.05(18), O3 – Mo1 – O1 107.4(2), O3 – Mo1 – O2 92.6(2), O3 – Mo1 – O4 104.1(2), O4 – Mo1 – O1 105.0(2), O4 – Mo1 – O2 161.5(2), O2 – Mo2 – O1 77.70(18), O5 – Mo2 – O1 162.7(2), O5 – Mo2 – O2 105.8(2), O6 – Mo2 – O1 90.7(2), O6 – Mo2 – O2 106.9(2), O6 – Mo2 – O5 104.0(2), N1 – Mo1 – N2 68.96(18), N4 – Mo2 – N3 69.16(19).

the combined effect of i) conformational rotations associated with the large and peripheral *tert*-butyl groups attached to the *N*,*N*′-chelated di-*t*Bu-bipy ligands, and ii) twisting around the central C – C bond of the organic molecule. A search in the literature and in the Cambridge Structural Database (Version 5.32, November 2011 with three updates [21]) revealed the existence of only a handful of related complexes with the same coordination environments for the Mo centers [5a–d], all crystallizing in either the space groups $P2_1/n$ or $P2_1/c$ (two alternate settings of the same space group). Remarkably, only $[Mo_2O_6(di\text{-}tBu\text{-}bipy)_2]$ reported herein is not truly centrosymmetric, illustrating well the significant structural influence of the various conformations that the di-*t*Bu-bipy organic ligands can adopt while coordinated to the metal centers.

$[Mo_2O_6(di\text{-}tBu\text{-}bipy)_2]$ is composed of two crystallographically distinct Mo centers, whose coordination polyhedra are edge-shared, a feature encountered in related molybdenum complexes [5]. The Mo···Mo separation in **1** is 3.1394(8) Å, which is within the range found in the aforementioned related compounds (ca. 3.12–3.18 Å). Mo1 and Mo2 exhibit almost similar highly distorted octahedral coordination environments, $\{MoN_2O_4\}$: besides the two terminal oxo groups, each metal center is further coordinated to two μ_2-bridging oxo moieties and one *N*,*N*′-chelated di-*t*Bu-bipy ligand (Fig. 1). Because the terminal oxo groups markedly exert the well-known *trans* influence in the coordination environments (i.e., each Mo is displaced from the geometrical center of the coordination polyhedron, leading to long *trans* connections to the oxo groups), the overall geometry is highly distorted for both Mo: on the one hand, the Mo – (N,O) bond lengths are found in the 1.707(4) to 2.339(5) Å range, and, on the other, the *cis*- and *trans*-(N,O) – Mo – (N,O) octahedral angles fall within the relatively wide 68.96(18)–107.4(2)° and 152.3(2)–162.7(2)° ranges, respectively (Fig. 1). The extreme values between which all registered lengths and angles vary were mainly observed for Mo1. This distortion seems to compensate the high planarity of the two coordinated aromatic rings: indeed, while the two pyridine rings coordinated to Mo1 are mutually rotated by only ca. 3.5°, the analogous value for Mo2 is nearly four times larger (ca. 11.9°); as a consequence, the steric pressure imposed on Mo1 seems to be higher, leading to a more distorted coordination environment.

The two water molecules of crystallization are engaged in strong ($d_{D\cdots A}$ usually below 3 Å, Table 1) and highly directional [<(DHA) usually above ca. 150°] O – H···O hydrogen bonding interactions with the dinuclear $[Mo_2O_6(di\text{-}tBu\text{-}bipy)_2]$ complexes, ultimately describing two $R^4_4(16)$ graph set motifs [22] which alternate along the [100] direction of the unit cell (Fig. 2). This arrangement leads to the formation of a one-dimensional supramolecular tape which close packs in a typical herringbone fashion in the *bc* plane of the unit cell to yield the crystal structure of **1** (Fig. 3). Water molecules of a given tape are further interacting with the coordinated di-*t*Bu-bipy ligands from an adjacent tape by way of several weak C – H···O interactions (not shown, see Table 1 for geometrical details). Indeed, even though the internuclear C···O distances are relatively long (varying between ca. 3.31 and 3.49 Å), the <(DHA) interaction angles for these connections are very close to linearity (all above ca. 167°), which clearly confirms their structural relevance in the crystal packing of **1**. Other intermolecular C – H···O contacts exist in the structure (last three entries in Table 1) which, despite their low directionality, help to strengthen the connections between neighboring complexes.

Table 1
Geometrical details of the hydrogen bonds and intermolecular close contacts present in **1**.[a]

D – H···A	d(D···A)/Å	<(DHA)/°
O1W – H1X···O5^{i}	2.789(7)	174(6)
O1W – H1Y···O5^{ii}	3.021(7)	148(5)
O2W – H2X···O6^{iii}	2.778(6)	173(6)
O2W – H2Y···O4^{ii}	2.843(7)	169(6)
C4 – H4···O1W^{iv}	3.491(8)	168
C22 – H22···O2W^{v}	3.415(8)	171
C25 – H25···O2W^{v}	3.314(8)	167
C1 – H1···O5^{vi}	3.306(9)	136
C9 – H9···O4^{vii}	3.306(9)	136
C19 – H19···O2^{vii}	3.090(8)	125

[a] Symmetry transformations used to generate equivalent atoms: (i) $1+x, 1+y, z$; (ii) $1-x, 1-y, 2-z$; (iii) $x, 1+y, z$; (iv) $-½+x, ½-y, ½+z$; (v) $½-x, -½+y, 1.5-z$; (vi) $-x, -y, 2-z$; (vii) $1-x, -y, 2-z$.