Inorganic Chemistry Communications 32 (2013) 59–63

Contents lists available at SciVerse ScienceDirect

Inorganic Chemistry Communications

journal homepage: www.elsevier.com/locate/inoche

A dinuclear oxo-bridged molybdenum(VI) complex containing a bidentate pyrazolylpyridine ligand: Structure, characterization and catalytic performance for olefin epoxidation

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ARTICLE INFO

Article history:
Received 20 February 2013
Accepted 24 March 2013
Available online 29 March 2013

Keywords:
Molybdenum
Dinuclear complexes
Pyrazolylpyridine ligands
Olefin epoxidation

ABSTRACT

The oxo-bridged dinuclear complex $[Mo_2O_4(\mu_2\text{-}O)Cl_2(pypzEA)_2]$ (**2**) (pypzEA = ethyl[3-(pyridin-2-yl)-1*H*-pyrazol-1-yl]acetate) was obtained upon the treatment of $[MoO_2Cl_2(pypzEA)]$ (**1**) with ethanol. The molecular structure of **2** consists of two highly distorted $\{MoClN_2O_3\}$ octahedra sharing a corner oxygen atom, with a Mo–O–Mo "kink" angle of 163.2(2)° and a Mo···Mo separation of 3.7029(7) Å. Catalytic results with **2** for the epoxidation of *cis*-cyclooctene using *tert*-butylhydroperoxide as oxidant compare favorably with those reported for related oxomolybdenum(VI) complexes. The reaction is homogeneous in nature, and a fraction of **2** dissolves and is converted to other types of soluble active species, one of which was isolated and identified as the oxodiperoxo complex $[MoO(O_2)_2(pypzEA)]$ (**3**).

Dioxomolybdenum(VI) complexes of the type $[MoO_2Cl_2(L)_n]$, where L is a monodentate (n = 2) or bidentate (n = 1) oxygen or nitrogen donor ligand, can exhibit excellent catalytic performance for the liquid-phase epoxidation of olefins using *tert*-butylhydroperoxide (TBHP) as oxidant [1,2]. Of critical importance is the stability of the complexes under the reaction conditions used. Previous studies have shown that the Mo–Cl bond is susceptible to cleavage (especially if no special measures are taken to exclude water from the reaction system), frequently leading to oxo-bridged dinuclear complexes. Thus, when the complexes $[MoO_2Cl_2(L)_2]$ bearing *N*,*N*-dialkylamides were examined as catalysts for the epoxidation of *cis*-cyclooctene, dioxo(*μ*-oxo)molybdenum(VI) complexes of the type $[Mo_2O_4(\mu_2\text{-}O)Cl_2(L)_4]$ were formed, probably because of the presence of up to 4% water in the decane solution of TBHP [3]. Recrystallization of $[MoO_2Cl_2(pzpy)]$ (pzpy = 2-[3(5)-pyrazolyl]pyridine) gave $[Mo_2O_4(\mu_2\text{-}O)Cl_2(pzpy)_2]$ [4], and the treatment of MoO_2Cl_2 with 2 equiv of pyrazole (pzH) monohydrate gave $[Mo_2O_4(\mu_2\text{-}O)Cl_2(pzH)_4]$ instead of mononuclear $[MoO_2Cl_2(pzH)_2]$ [5]. Similarly, for the reaction of $[MoO_2Cl_2(H_2O)_2]\cdot Et_4NCl$ with 1 equiv of 4,4′-di-*tert*-butyl-2,2′-bipyridine (di-*t*Bu-bipy), mononuclear $[MoO_2Cl_2(\text{di-}t\text{Bu-bipy})]$ was obtained when the reaction was run in CH_2Cl_2, whereas the oxo-bridged complex $[Mo_2O_4(\mu_2\text{-}O)Cl_2(\text{di-}t\text{Bu-bipy})_2]$ was the only reaction product obtained in a CH_2Cl_2/H_2O biphasic system [6].

Several higher nuclearity oxomolybdenum(VI) compounds have been isolated after the reaction of dichlorodioxomolybdenum(VI) complexes with excess water, namely the polymeric materials $\{[MoO_3(2,2'\text{-bipyridine})][MoO_3(H_2O)]\}_n$ [7] and $[Mo_2O_6(HpypzA)]$ (HpypzA = [3-(pyridinium-2-yl)-1*H*-pyrazol-1-yl]acetate) [8], and the octanuclear complex $[Mo_8O_{22}(OH)_4(\text{di-}t\text{Bu-bipy})_4]$ [9]. The material $[Mo_2O_6(HpypzA)]$ was obtained from $[MoO_2Cl_2(pypzEA)]$ (pypzEA = ethyl[3-(pyridin-2-yl)-1*H*-pyrazol-1-yl]acetate), which was previously shown to be an effective homogeneous catalyst for the epoxidation of olefins [10,11].

In the present work the stability of $[MoO_2Cl_2(pypzEA)]$ (**1**) was further examined by treating the complex with ethanol. The reactivity of dichlorodioxomolybdenum(VI) complexes towards alcohols is of interest due to the fact that when TBHP is used as the oxidant in catalytic olefin epoxidation, *tert*-butanol is formed as the end-product after oxygen transfer. We anticipated that molybdenum(VI) oxoalkoxide complexes might form upon the reaction of **1** with ethanol [12–15]. However, the dinuclear complex $[Mo_2O_4(\mu_2\text{-}O)Cl_2(pypzEA)_2]$ (**2**) was instead isolated from the solution of **1** in ethanol (Scheme 1) [16]. Herein we report the characterization of **2** and its single crystal X-ray structure, and preliminary studies using the complex as a catalyst in the epoxidation of *cis*-cyclooctene.

Powder X-ray diffraction studies, alongside elemental CHN analyses, unequivocally confirmed the phase purity and homogeneity of the bulk material (please see the Supplementary data for details, Figs. S1 and S2). In the FT-IR spectrum of **2**, the pair of intense bands at 910 and 944 cm^{-1} is assigned to the asymmetric and symmetric stretching vibrations of the *cis*-$[MoO_2]^{2+}$ unit (Fig. S3). These bands are shifted to higher frequency when compared with those for the mononuclear complex **1** (900 and 937 cm^{-1}), which points to a

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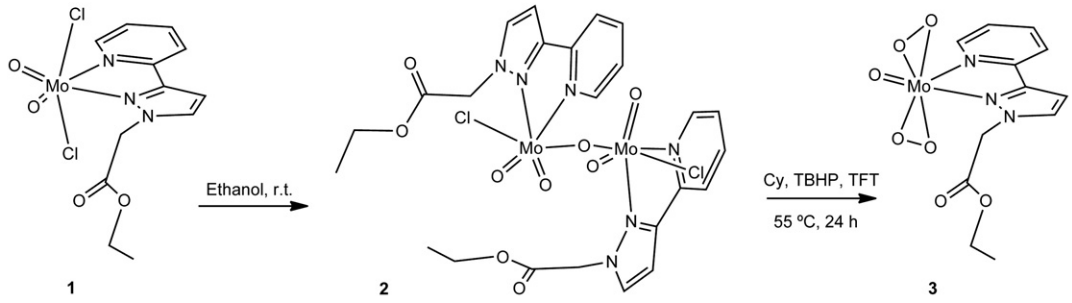
http://dx.doi.org/10.1016/j.inoche.2013.03.028



Scheme 1. Isolation of complexes **2** and **3** starting from **1**.

strengthening of the Mo=O bonds in **2**. A very strong band centered at 783 cm^{-1} is attributed to a ν(Mo–O–Mo) stretching mode overlapping with a ligand mode (complex **1** exhibits a strong band at 775 cm^{-1}). Towards higher frequencies complex **2** exhibits additional pypzEA bands at 1569 and 1612 cm^{-1} (C–C inter-ring and C–N/C–C ring stretching modes [4,11]), and 1731 and 1735 cm^{-1} (ν(C=O)). The appearance of two ν(C=O) bands for **2** vs. only one band for **1** (at 1743 cm^{-1}) is consistent with the single crystal X-ray diffraction (XRD) structure (described below), which revealed these functional groups to be crystallographically nonequivalent. By contrast, the solution ^1H and ^{13}C NMR spectra of **2** in deuterated dimethylsulfoxide show only one set of signals for the organic ligand, indicating that the dinuclear complex may adopt average C_2 symmetry in solution.

Single-crystal XRD studies [17] revealed that compound **2** crystallizes in the centrosymmetric space group $P\bar{1}$ [18] with the asymmetric unit being composed of a whole $[Mo_2O_4(\mu_2\text{-}O)Cl_2(pypzEA)_2]$ molecular unit as depicted in Fig. 1. The crystallographically independent neutral dinuclear complex present in **2** exhibits a pseudo-C_2 symmetry for its $\{Mo_2Cl_2N_4O_5\}$ inorganic core, but the overall crystal symmetry does not reflect this local feature. This occurs because of the considerable conformational flexibility of the pendant groups attached to the pyrazolylpyridine ligand, which permits a rotation about the N–C bond to the five-membered ring, leading to a disruption of the symmetry and a dinuclear unit based on two crystallographically distinct Mo^{6+} centers (see below). This structural feature is not in line with that usually reported in the literature [28] for related dinuclear complexes based on $\{Mo_2N_4O_6\}$ cores [29], for which $[Mo_2O_6(\text{di-}t\text{Bu-bipy})_2]$ is a notable exception [30]. Conversely, for closely-related dinuclear units based on $\{Mo_2X_2N_4O_5\}$ cores (X being a halogen) [4,31], the loss of centrosymmetry is not so uncommon and has been previously reported for analogous dinuclear complexes containing 2-[3(5)-pyrazolyl]pyridine and di-*t*Bu-bipy *N*,*N*′-chelated organic ligands.

The two crystallographically independent Mo^{6+} centers exhibit highly distorted octahedral coordination environments, $\{MoClN_2O_3\}$. As depicted in Fig. 1, the μ_2-bridging oxo group is responsible for the formation of the dinuclear unit, which is based on the corner-sharing of two $\{MoClN_2O_3\}$ octahedra. While the apical positions of the $\{MoClN_2O_3\}$ octahedra are occupied by the chloro atoms and the μ_2-bridging oxo group, the equatorial planes are instead occupied by the *N*,*N*′-chelated pypzEA ligands and the terminal oxo groups.

These latter groups markedly exert their well-known *trans* effect in the octahedral coordination environments, with the Mo1 and Mo2 centers being displaced by *ca.* 0.47 Å from the geometrical center of the coordination polyhedron. The refined Mo–(Cl,N,O) bond lengths range from 1.688(3) to 2.4156(14) Å (see caption of Fig. 1), and the *cis*- and *trans*-(Cl,N,O)–Mo–(Cl,N,O) octahedral angles are found in the relatively wide 68.52(13)–106.36(18)° and 155.48(11)–162.72(15)° ranges, respectively (see Table S1 in the Supplementary data). The μ_2-bridging oxo group imposes a Mo···Mo separation of 3.7029(7) Å and a Mo–O–Mo "kink" angle of 163.2(2)°. A search in the literature for the analogous values in closely-related dinuclear units based on $\{Mo_2X_2N_4O_5\}$ cores [31] reveals that those registered for compound **2** are typical: the known intermetallic distances range from *ca.* 3.62 to 3.75 Å, and the angles imposed by the μ_2-bridging oxo groups are found in the *ca.* 144–180° range. The "kink" angle registered for **2** is the largest reported for non-centrosymmetric dinuclear units (*ca.* 144° for the complex with di-*t*Bu-bipy [31a] and *ca.* 156° for that with 2-[3(5)-pyrazolyl]pyridine [31b]), approaching linearity as in centrosymmetric complexes.

Individual dinuclear $[Mo_2O_4(\mu_2\text{-}O)Cl_2(pypzEA)_2]$ complexes close pack in the solid state to form the crystalline structure of compound **2** (Fig. 2b) mediated by a significant number of distinct supramolecular contacts. Those that are structurally more significant concern the offset π–π contacts between neighboring complexes along the [100] direction of the unit cell (inter-centroid distance of 3.720(3) Å — Fig. 2a). These interactions lead to the formation of a supramolecular columnar arrangement of complexes, which segregates to the one side the alkyl

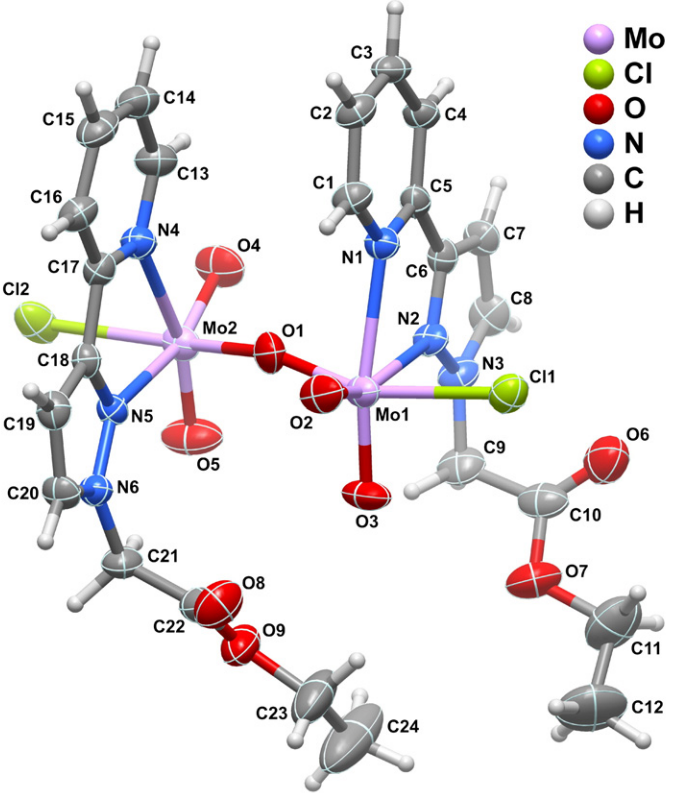


Fig. 1. Schematic representation of the $[Mo_2O_4(\mu_2\text{-}O)Cl_2(pypzEA)_2]$ molecular unit present in **2** showing the labeling scheme for all non-hydrogen atoms, which are represented as thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are represented as small spheres with arbitrary radii. Selected bond lengths (Å): Mo1–O1 1.867(3), Mo1–O2 1.689(3), Mo1–O3 1.700(3), Mo1–N1 2.356(4), Mo1–N2 2.331(4), Mo1–Cl1 2.4156(14), Mo2–O1 1.876(4), Mo2–O4 1.688(3), Mo2–O5 1.703(4), Mo2–N4 2.346(4), Mo2–N5 2.358(4), Mo2–Cl2 2.4035(14). Selected bond angles are given in Table S1 in the Supplementary data.