

Synthesis of bis[N,O-{2'-pyridyl-methanolate}]dioxomolybdenum(VI) epoxidation catalyst and novel crystal structure derived from X-ray diffraction and DFT calculations

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Abstract

The bis[N,O-{2'-pyridyl-methanolate}] dioxomolybdenum(VI) complex was synthesized and its crystal structure determined by X-ray diffraction (XRD), and then confirmed by theoretical DFT calculations. This complex was subsequently used in the epoxidation reaction of 1-octene with ethylbenzene hydroperoxide in liquid phase and it showed slightly better performance than the molybdenum acetylacetonate complex as reference.

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1. Introduction

Epoxides, in particular propylene oxide, are useful compounds that have found applications in diverse areas. Many different methods for the preparation of epoxides have been developed, but the most extensive industrial method is the oxidation of alkenes to the corresponding epoxide in liquid phase with organic hydroperoxides in the presence of a catalyst. Indeed, hydrocarbon-soluble organometallic compounds of the transition metals can be employed as homogeneous catalysts. Examples are vanadium or molybdenum compounds [1]. Epoxide selectivity depends on the Lewis acidity and the oxidation state of the metals [1,2]. Thus, molybdenum-containing catalysts are best for this process [3], and most of them have been synthesized from dioxo-bis(acetylacetonate) of molybdenum(VI), which itself shows good catalytic properties in oxidation reactions [4]. Some reports have addressed molybdenum complexes whose ligands contain donor atoms such as oxygen and nitrogen [5] or bis-nitrogen [6]. The first X-ray crystal structure of

a [MoO₂X₂L₂]-type complex was reported in 1966. [7] [MoO₂X₂L₂] complexes are monomeric and present a distorted octahedral geometry, with the oxo-ligands *cis* to each other in order to maximize backdonation into the empty t_{2g} set orbitals [8]. In general, these types of compounds show good performance as catalysts in the epoxidation reaction of olefins in liquid phase, using organic hydroperoxides as oxidant agents.

This communication describes the preparation and structural characterization of the bis[N,O-{2'-pyridyl-methanolate}] dioxomolybdenum(VI) complex (MoPym₂) by means of X-ray diffraction (XRD), confirmed by theoretical DFT calculations.

2. Experimental

Reagents were commercial samples and were not purified further.

The MoPym₂ complex was prepared as follows: a solution of 2-pyridylmethanol (2.5 g and 0.023 moles) and ammonium heptamolybdate (2 g and 0.0115 moles of Mo) in 20 ml of distilled water was refluxed for 1 h. The precipitate obtained was filtered, repeatedly washed with dichloromethane

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and water, and then dried in an oven at 335 K. Finally, the solid was recrystallized by dissolving it in dichloromethane and cooling solution at 253 K. Under these conditions, stable crystals of the complex were obtained.

Elemental analyses were carried out on a Perkin Elmer 2400 CHN device and Mo contents were measured on a Perkin Elmer 3300 ICP-AES apparatus.

X-ray structural determination were carried out with a transparent fresh crystal coated with perfluoropolyether vacuum-pump oil and mounted in a Bruker-Siemens diffractometer equipped with a CCD detector and low-temperature device. More than a hemisphere of the reciprocal space was explored by a combination of three exposure sets, using Mo K_{α} radiation ($\lambda = 0.71069 \text{ \AA}$) at 273 K. The structure of the complex was solved by direct methods and refined by full matrix least-squares calculations, using anisotropic thermal parameters for non-hydrogen atoms and isotropic for H atoms. The solution and refinement were made by the use of the SHELXTL software package [9].

DFT full-geometry optimizations of the MoPym₂ complex were performed at the unrestricted density functional B3LYP [10] level using the Gaussian 98 A.11 version suite of programs [11]. The LANL2DZ [12] basis set was used for orbital expansion to solve the Kohn–Sham equations.

Catalytic epoxidation of oct-1-ene with ethylbenzene hydroperoxide (EBHP) was carried out in a glass batch-reactor equipped with a magnetic stirrer and a condenser. In a typical run, 44.8 g of alkene (0.4 mol) and 33 g of a solution of EBHP (33 wt.%) in ethylbenzene (0.08 mol of EBHP) were heated to 367 K, after which an amount of catalyst corresponding to 40 ppm of molybdenum was added. The concentration of EBHP was measured by standard iodometric titration. The remaining organic compounds were analyzed by GC-FID on a Hewlett Packard 6890-plus device equipped with an HP-WAX capillary column.

3. Results and discussion

The reaction of 2-pyridylmethanol with ammonium heptamolybdate in molar ratio of 2:1 gave a white complex. The elemental analyses revealed that the synthesized complex fits in well with the stoichiometry of one molybdenum and two ligands (theoretical composition: Mo 27.9%, C: 41.9%, H: 3.5%, and N: 8.1%, experimental composition: Mo 26.9%, C: 41.0%, H: 3.2%, and N: 8.0%).

The molecular structure was determined by single-crystal X-ray diffraction on a crystal selected from the recrystallized in dichloromethane product. On determining the structure¹, the composition was found to be MoPym₂·H₂CCl₂ [Pym = N,O-{2'-pyridyl-methanolate}] (Crystal data for

MoPym₂·H₂CCl₂ (bis[N,O-{2'-pyridyl-methanolate}]) dioxomolybdenum(VI) H₂CCl₂: orthorhombic, space group Pbc_a, $a = 12.2233(13)$, $b = 15.8278(17)$, and $c = 17.1892(18) \text{ \AA}$, $V = 3325.6(6) \text{ \AA}^3$, $Z = 8$, $M_w = 429.1$, $D_c = 1.714 \text{ Mg cm}^{-3}$, and $\mu(\text{Mo } K_{\alpha}) = 1.127 \text{ mm}^{-1}$). In air, the crystals decompose very quickly losing crystallinity and transparency, although they conserve their morphology. The dichloromethane molecules, which probably act as templates in the structure (Fig. 1a), are situated in the middle of tunnels parallels to the a -direction. No appreciable interaction with neighboring molecules was observed, and

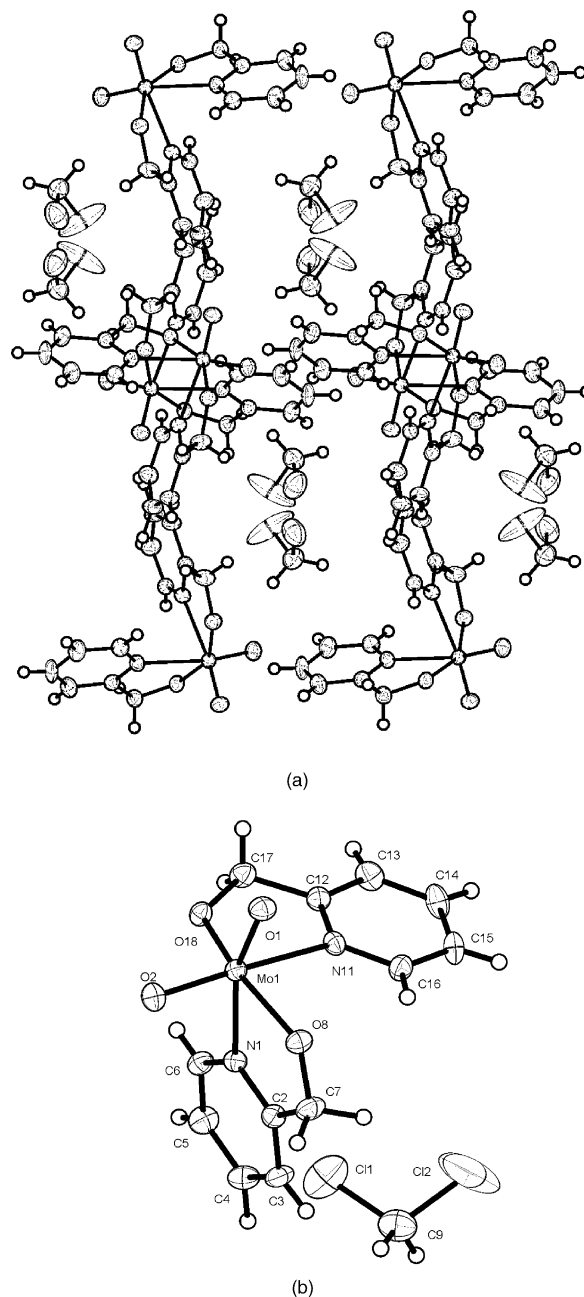


Fig. 1. ORTEP drawing of MoPym₂·H₂CCl₂ crystal structure along (a); asymmetric unit representation (b).

¹ CCDC reference number 205868. Supplementary data for crystallographic data in CIF or other electronic format are available from the authors.

Table 1
Selected bond lengths and angles determined by X-ray structure and DFT geometrical optimization

	Bond lengths (pm)			Angles (°)	
	Experimental	DFT		Experimental	DFT
Mo(1)–O(2)	171.3(2)	174.1	O(2)–Mo(1)–O(1)	105.73(10)	107.54
Mo(1)–O(1)	171.6(2)	174.1	N(1)–Mo(1)–O(1)	163.31(9)	165.08
Mo(1)–N(1)	233.1(2)	240.2	N(1)–Mo(1)–O(2)	88.19(9)	85.80
Mo(1)–O(8)	194.0(2)	198.1	N(1)–C(2)–C(7)	114.9(3)	113.76
Mo(1)–O(18)	193.7(2)	198.1	C(2)–N(1)–Mo(1)	113.60(19)	112.88
N(1)–C(2)	133.2(4)	135.6	O(8)–C(7)–C(2)	111.2(2)	110.08
C(2)–C(7)	150.1(4)	152.1	N(11)–Mo(1)–O(18)	73.27(8)	71.57
O(8)–C(7)	140.7(4)	143.7	N(11)–Mo(1)–O(2)	161.98(9)	164.95
Mo(1)–N(11)	235.7(2)	241.2	N(11)–Mo(1)–O(1)	90.33(9)	85.83
N(11)–C(12)	133.9(4)	135.5	N(11)–C(12)–C(17)	114.8(3)	113.75
C(12)–C(17)	149.8(4)	152.1	C(12)–N(11)–Mo(1)	112.76(18)	113.01
O(18)–C(17)	141.2(4)	143.7	O(18)–C(17)–C(12)	111.4(2)	110.02

Values in parenthesis are standard deviations.

thus, solvent molecules are easily lost, making the structure vulnerable to moisture and air or oxygen. The molecule (Fig. 1b) is similar to those found in other dioxomolybdenum complexes with (2'-pyridyl)alcoholates [5d, e].

This structure was fully corroborated by DFT geometrical optimization calculations. The values of bond lengths and angles calculated virtually coincided with the corresponding values determined experimentally by X-ray diffraction (Table 1).

The molybdenum complex was tested in the epoxidation reaction of 1-octene with EBHP and the results were compared with the reference MoO₂(acac)₂. Activity, expressed as turnover frequency (TOF = moles of 1-octene converted per Mo atom and per minute) was somewhat higher for the MoPym₂ complex as expected than for the MoO₂(acac)₂ reference catalyst (Table 2).

The reaction was selective to epoxide since in both cases the only product detected from the oct-1-ene was 1,2-epoxyoctane. The selectivity based on the EBHP consumed at a level of conversion of 96 was fairly high (82–83%) for both systems (Table 2).

In the light of the results presented in this work, it can be concluded that the synthesis of the MoPym₂ complex can be safely accomplished by means of a simple procedure consisting the reaction of ammonium heptamolybdate with 2-pyridylmethanol in an aqueous phase. It was found that its recrystallization in dichloromethane results in the MoPym₂·H₂CCl₂ compound, in which the dichloromethane act as templates of the structure. The DFT calculations

proved to be in excellent agreement with all the diffraction data. Finally, the MoPym₂ complex reported here displayed high activity (TOF value slightly higher than that of the Mo(acac)₂ reference) in the epoxidation reaction of 1-octene and had a high efficiency in EBHP conversion.

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Table 2
Catalyst performance in the epoxidation of oct-1-ene at 367 K

Catalyst	TOF (min ⁻¹) ^a	Percent conversion of 1-octene (2 h)	Percent selectivity ^b to 1,2-epoxyoctane
MoO ₂ (acac) ₂	273	15.9	83
MoPym ₂	293	15.7	82

^a Extrapolated to time 0.

^b Selectivity based on EBHP consumed, at 96% conversion level.

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