Molecular Structure of the Molybdenum Oxo-Diperoxo Compound $MoO(O_2)_2(OPy)(H_2O)$: A Computational and X-ray Study

Fabrício R. Sensato,[†] Quezia B. Cass,[†] Elson Longo,[†] Julio Zukerman-Schpector,[†] Rogerio Custodio,[‡] Juan Andrés,[§] Marcelo Zaldini Hernandes,[||] and Ricardo L. Longo*,[||]

Departamento de Química, Universidade Federal de São Carlos, CP 676, 13565-905, São Carlos, SP, Brazil, Instituto de Química, Departamento Físico-Química, Universidade Estadual de Campinas, CP 6154, 13083−970, Campinas, SP, Brazil, Departament de Ciènces Experimentals, Universitat Jaume I, Apartat 224, 12080 Castelló, Spain, and Departamento de Química Fundamental, Universidade Federal de Pernambuco, 50740−540 Recife, PE, Brazil

Received January 4, 2001

We have carried out a combined experimental and theoretical study of the molecular structure of the $MoO(O_2)_2(OPy)(H_2O)$ coordination compound using X-ray crystallography and DFT-B3LYP computational method, respectively. The $MoO(O_2)_2(OPy)(H_2O)$ complex crystallizes in the orthorhombic space group *Pmna* with $Z = 4$, $a = 6.9001(9)$ Å, $b = 8.0471(1)$ Å, $c = 16.227(2)$ Å, $V = 901.0(2)$ Å^3, and the X-ray data analysis yields a bipyramidal-pentagonal coordination polyhedron for the Mo atom. The pyridine *N*-oxide (OPy) ligand occupies the equatorial position, with the oxygen atom of this ligand being located in the same plane as the four peroxo oxygen atoms. The H_2O ligand is situated trans to the oxo group, forming intermolecular hydrogen bonds with peroxo groups belonging to two adjacent complexes. In our theoretical approach these intermolecular interactions were taken into account by including two methanol molecules which form hydrogen bonds with the water ligand leading to a good agreement between the calculated and the experimental geometry. Our results suggest that it is necessary to take into account the presence of these interactions in order to reconcile the theoretical results to the experimental data, in particular the distance between Mo and the oxygen of water ligand. These results seem to be a general feature for analogous bis-peroxo complexes that have been reported in the literature.

1. Introduction

Since the seminal works by Mimoun,[1−3] the search for selective oxidation reagents is a very important goal in many reaction development researches due to their impact in chemical synthesis. In particular, oxo-diperoxo complexes of transition metals with general formula $MO(O_2)_2L_1L_2$ (M = Mo, W, Re) are an important class of compounds that has been used in the oxidation of a variety of organic substrates.[4−6] The importance of these compounds is related to their versatility, since a variety of ligands L_1 and L_2 can be employed allowing for a fine control of their reactivity.

Molybdenum oxo-peroxo complexes, known as Mimoun complexes (for reviews see refs 7−9), present a trigonal bipyramid coordination polyhedron for the Mo atom with the oxo group in the apical position trans to one of the L_1 or L_2 ligand, with the other ligand occupying the equatorial position together with the peroxo groups.[10−13] In particular, the complex $MoO(O_2)_2(OPy)(H_2O)$, where OPy = pyridine *N*-oxide ligand, was first synthesized by Mimoun et al.[1] and characterized by infrared spectroscopy[1]; while Westland et al.[14] carried out a comparative study of rate of O_2 evolution for a variety of diperoxo complexes of formula $MO(O_2)_2L_1L_2$ (M = Mo or W) stabilized by oxides of amines, phosphines, and arsines. However, to our knowledge, there is no experimental neither theoretical structure determination of this coordination compound.

The $MoO(O_2)_2(OPy)(H_2O)$ complex has been shown to be a very effective agent for oxygen transfer reactions of a wide class of substrates, including the oxidation of a series of sulfides to sulfoxides.[15] Thus, the determination of its molecular and electronic structure could yield some insight into its catalytic activity. Thus, computational methods as well as X-ray structure analysis have been used to study this complex. There is a possibility that the oxo and/or the peroxo groups of a complex

---

* Corresponding author. Fax: +55 81 3271 8442. Tel: +55 81 3271 8443. e-mail: longo@npd.ufpe.br.

[†] Universidade Federal de São Carlos.

[‡] Universidade Estadual de Campinas.

[§] Universitat Jaume I.

[||] Universidade Federal de Pernambuco.

(1) Mimoun, H.; De Roch, I. S.; Sajus, L. *Bull. Soc. Chim. Fr.* **1969**, 1481.
(2) Mimoun, H.; De Roch, I. S.; Sajus, L. *Tetrahedron* **1970**, *26*, 37.
(3) Mimoun, H. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 734.
(4) Thiel, W. R.; Priermeier, T. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1737.
(5) Thiel, W. R.; Angstl, M.; Hansen, N. *J. Mol. Catal. A: Chem.* **1995**, *103*, 5
(6) Thiel, W. R. *J. Mol. Catal. A: Chem.* **1997**, *117*, 449.
(7) Dickman M. H.; Pope, M. T. *Chem. Rev.* **1994**, *94*, 569.
(8) Jorgensen, K. A. *Chem. Rev.* **1989**, *89*, 431.
(9) Morris, M. J. *Coord. Chem. Rev.* **1996**, *152*, 309.
(10) Le Carpentier, J. M.; Schlupp, R.; Weiss, R. *Acta Crystallogr.* **1972**, *B28*, 1278.
(11) Schlemper, E. O.; Schrauzer, G. N.; Hughes, L. A. *Polyhedron* **1984**, *3*, 377.
(12) Griffith, W. P.; Slawin, A. M. Z.; Thompson, K. M.; Williams, D. *J. Chem. Soc., Chem. Commun.* **1994**, 569.
(13) Martín-Zarza, P.; Gili, P.; Rodriguez-Romero, V.; Ruiz-Pérez, C.; Solans, X. *Inorg. Chim. Acta* **1994**, *223*, 173.
(14) Westland, A. D.; Haque, F.; Bouchard, J. *Inorg. Chem.* **1980**, *19*, 2255.
(15) Hernandes, M. Z. M. Sc. thesis, Universidade Federal de São Carlos 1998.

10.1021/ic010020h CCC: $20.00

might form hydrogen bond with the water molecule of an adjacent complex in the crystal. Raman infrared spectra and ^{13}C NMR data for other comparable complexes suggest that the $MoO(O_2)_2(OPy)(H_2O)$ compound should retain its solid-state structure in solution. Therefore, the water ligand should form hydrogen bonds with Lewis base solvents, such as, alcohols. As far as we know, this is the first study of the effects of the intermolecular hydrogen bond formation on the molecular structure of the Mimoun complexes. This could lead to important information about the intermolecular interactions on the molecular structure, which could have consequences for the reactivity of these catalysts.

The following section describes the experimental and theoretical procedures. In Section 3, the results are presented, analyzed, and discussed, followed by a section of conclusions.

2. Experimental and Theoretical Procedures

The preparation of the $MoO(O_2)_2(OPy)(H_2O)$ complex followed the procedure proposed by Mimoun[1−3,15] and the single crystals were obtained from an aqueous/2-propanol solution.

2.1. Crystal Structure Analysis. An irregular yellow crystal was mounted at random on an CAD4-Mach3 Enraf-Nonius diffractometer. Cell dimensions were determined by least-squares fit on the setting angles for 25 reflections ($7.23° < \theta < 15°$). Intensity measurements were carried out using the $\theta/2\theta$ scan mode and graphite monochromated Mo Kα ($\lambda = 0.71073$ Å) radiation. The intensities of three standard reflections varied by ca. 1% throughout the experiment. Data were corrected by Lorentz, polarization and absorption effects (maximum and minimum transmission factors being 0.8670 and 0.7577, respectively). The structure was solved by the Patterson heavy-atom-method and difference Fourier calculations. The following programs were used: structure solution SHELXS-86;[16] refinement SHELXL-97;[17] and graphic presentation ZORTEP[18] and ORTEP-3.[19]

2.2. Theoretical Calculations and Model System. We carried out density functional calculations employing the hybrid B3LYP scheme to describe the exchange-correlation contribution to the electron−electron interaction[20,21] implemented into the GAUSSIAN 98 program.[22] The minimum in the potential energy surface was characterized by the absence of negative force constants,[23] and no symmetry restrictions were imposed during the geometry optimization procedure. The standard 6-31G(d,p) basis set was employed for C, N, and H atoms[24] while an uncontracted basis set (11s5p2d) was used to represent the oxygen centers. For the Mo center we have used a valence basis set (8s6p7d1f) combined with RECP (quasi-relativistic effective core potential) of Hay and Wadt.[25] The all-electron basis set for O atoms and the valence basis set for Mo center were tailored with the application of the Generator Coordinate Method[26,27] which has been employed successfully to investigate the electronic structure of atoms and molecules (see refs 28−31 and references therein). The corresponding exponents as well as the procedure employed to generate a truncated valence basis set to be used with the RECP are described in details in our previous theoretical study.[32] The intermolecular interactions were simulated by two methanol molecules placed in such a positions that were able to form hydrogen bonds with the water molecule ligand.

Table 1. Crystal Data and Structure Refinement for $MoO(O_2)_2(OPy)(H_2O)$ Complex[a]

empirical formula	$C_5H_7MoNO_7$
formula weight	289.06
temperature	291(1) K
wavelength	0.71073 Å
crystal system, space group	orthorhombic, *Pmna*
unit cell dimensions	$a = 6.9001(9)$ Å
	$b = 8.0471(1)$ Å
	$c = 16.227(2)$ Å
volume	901.0(2) $Å^3$
Z, calcd density	4, 2.130 mg m^{-3}
absorption coefficient	1.469 mm^{-1}
F(000)	568
crystal size	0.20 × 0.15 × 0.10 mm
θ range for data collection	3.21−25.0°
limiting indices	$0 \leq h \leq 8$, $0 \leq k \leq 9$, $-19 \leq l \leq 0$
reflections collected/unique	852/852
refinement method	Full-matrix least-squares on F^2
data/restraints/parameters	852/0/73
goodness-of-fit on F^2	1.130
final *R* indices [$I > 2\sigma(I)$]	R1 = 0.0285[b], wR2 = 0.0781[c]
R indices (all data)	R1 = 0.0341[b], wR2 = 0.0737[c]

[a] Ψ-scan absorption corrections was applied; $T_{max} = 0.867$ and $T_{min} = 0.758$ (North, A. C. T.; Phillips, D. C.; Mathews, F. S. *Acta Crystallogr.* **1968**, *A24*, 351). [b] $R1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. [c] $wR2 = [(\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2)]^{1/2}$.

3. Results and Discussion

The $MoO(O_2)_2(OPy)(H_2O)$ complex crystallizes orthorhombically in the space group *Pmna* with Z = 4, according to Table 1. The positional, isotropic, and anisotropic displacement parameters are presented in the Supporting Information. The X-ray molecular structure and the atomic labels are illustrated in the Figure 1. The molecules are hydrogen bonded producing chains parallel to *c* axis and are given in the Supporting Information.

Good agreement has been found between calculated and X-ray experimental results for the crystal structure of $MoO(O_2)_2(OPy)(H_2O)$ compound except for geometric parameters that define the relative position of the H_2O ligand, namely, the Mo−O(19) bond distance is clearly overestimated by our calculations (exp 2.298 Å and calcd 2.811 Å), while the distance between hydrogen atoms of water and the peroxo oxygen is underestimated (see Table 2). A similar disagreement has been

---

(16) Sheldrick, G. M. *SHELXS86 − Program for the Solution of Crystal Structures*. University of Gottingen, Germany. 1986.
(17) Sheldrick, G. M. *SHELXL97 − Program for the Refinement of Crystal Structures*. University of Gottingen, Germany. 1997.
(18) Zsolnai, L. *ZORTEP − An Interactive Molecular Graphics Program*. University of Heidelberg, Germany. 1995.
(19) Farrugia, L. J. *J. Appl. Crystallogr.* **1997**, *30*, 565.
(20) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098.
(21) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.
(22) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.1; Gaussian, Inc.: Pittsburgh, PA, 1998.
(23) Foresman, J. B.; Frish, A. *Exploring Chemistry with Electronic Structure Methods*. Gaussian Inc., Pittsburgh, PA, 1993.
(24) Ditchfield, R.; Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* **1970**, *52*, 5001.
(25) Wadt, W. R.; Hay, P. J. *J. Chem. Phys.* **1985**, *82*, 284.
(26) Griffin, J. J.; Wheeler, J. A. *Phys. Rev.* **1957**, *108*, 311.
(27) Hill, D. L.; Wheeler, J. A. *Phys. Rev.* **1953**, *89*, 1102.
(28) Custodio, R.; Davis, W. M.; Goddard, J. D. *J. Mol. Struct. (THEOCHEM)* **1994**, *315*, 163.
(29) Giordan, M.; Custodio, R.; Morgon, N. H. *Chem. Phys. Lett.* **1997**, *279*, 396.
(30) Morgon, N. H.; Custodio, R.; Riveros, J. M. *Chem. Phys. Lett.* **1995**, *235*, 436.
(31) Morgon, N. H.; Custodio, R.; Tostes, J. G. R.; Taft, C. A. *J. Mol. Struct. (THEOCHEM)* **1995**, *335*, 11.
(32) Sensato, F. R.; Cass, Q. B.; Longo, E.; Hernandes, M. Z.; Longo, R. L.; Custodio, R.; Andres, J. *Theor. Chem. Acc.*, submitted.

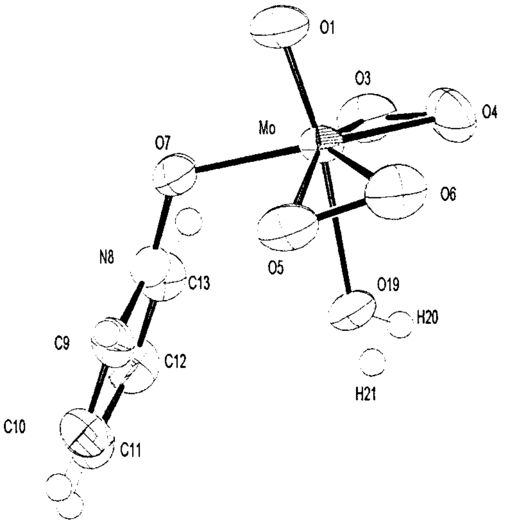

Figure 1. ORTEP drawing of the X-ray molecular structure and atomic labeling of $MoO(O_2)_2(OPy)(H_2O)$ (50.0% probability ellipsoids, except for the hydrogen atoms).

Table 2. Selected Bond Distances, Angles, and Dihedrals for the Isolated $MoO(O_2)_2(OPy)(H_2O)$ Complex (**I**) and $MoO(O_2)_2(OPy)(H_2O)-(CH_3OH)_2$ (**II**)[a]

	I (calcd)	**II** (calcd)	experimental
Mo−O(1)	1.676	1.681	1.670
Mo−O(3)	1.940	1.951	1.955
Mo−O(4)	1.949	1.937	1.919
Mo−O(5)	1.940	1.966	1.955
Mo−O(6)	1.949	1.943	1.919
Mo−O(7)	2.117	2.155	2.076
O(3)−O(4)	1.452	1.455	1.470
O(5)−O(6)	1.452	1.450	1.470
O(7)−N(8)	1.338	1.326	1.354
Mo−O(19)	2.811	2.330	2.295
H(20)−O(3)$_{\text{back-side}}$	2.489	2.533	2.718
H(21)−O(5)$_{\text{back-side}}$	2.486	2.657	2.718
H(20)−O(4)$_{\text{front-side}}$	2.249	2.749	2.833
H(21)−O(6)$_{\text{front-side}}$	2.245	2.733	2.833
O(1)−Mo−O(7)	96.3	90.5	89.2
O(3)−Mo−O(5)	143.0	152.3	156.7
O(4)−Mo−O(6)	89.5	90.3	88.9
O(3)−Mo−O(4)	43.8	43.9	44.6
O(5)−Mo−O(6)	43.8	43.5	44.6
O(1)−Mo−O(3)	108.1	103.6	101.6
O(1)−Mo−O(4)	107.9	105.0	102.8
O(1)−Mo−O(5)	108.1	103.7	101.6
O(1)−Mo−O(6)	107.9	104.6	102.8
Mo−O(7)−N(8)	118.1	122.5	123.0
O(1)−Mo−O(19)	177.8	169.5	170.8
O(1)−Mo-O(4)−O(3)	−97.7	−94.3	−93.5
O(1)−Mo-O(6)−O(5)	97.7	94.7	93.5
O(3)−O(4)-O(6)−O(5)	0.0	0.9	0.0
O(6)−O(4)-O(3)−Mo	19.5	14.6	12.7

[a] See Figure 1 for the definition of the atom labels. Bond distances in angstroms (Å) and angles in degrees.

reported by Rösch et al.[33] who have compared experimental and theoretical results for a related complex $ReO(O_2)_2(CH_3)(H_2O)$ (exp 2.25 Å and calcd 2.48 Å). More recently, the potential energy curve for NH_3−M bond in the $(NH_3)(L)M(O)_{2-n}(\eta^2\text{-}O_2)_{1+n}$ ($n = 0, 1$; L = none, NH_3; M = Cr, Mo, W) complexes has been inferred to be quite flat, so that small perturbations may cause large structural changes.[34] In addition, Frenking et al.[35] have studied the equilibrium geometry of the molybdenum oxo/peroxo compounds $MoO_n(O_2)_{3-n}$ and the related complexes $[MoO_n(O_2)_{3-n}(OPH_3)]$ and $[MoO_n(O_2)_{3-n}(OPH_3)(H_2O)]$ ($n = 0-3$) by DFT-B3LYP methods, and they also have found a similar discrepancy and partly attributed it to unspecified solid-state effects. Thiel et al.[36] have also found that the calculated distance between the axial ligand and the molybdenum atom is overestimated with respect to the corresponding distance for analogous molybdenum peroxo complexes. It should be noted that even in the experimental X-ray structure the $Mo-OH_2$ distance (2.295 Å) is reported to be distinctly longer than the Mo−OPy distance (2.076 Å). Difference between the axial and equatorial bond length has been reported to occur in related complexes and it has been proposed that it is due to the trans influence of the oxo group, O(1).[4,11−13,15] The large difference 2.295 Å vs 2.076 Å observed in the complex studied here cannot, however, be explained solely on this effect. The significant discrepancy between the calculated and the experimental results for only this $Mo-OH_2$ bond distance suggests that another effects should be present. Thus, upon examination of the X-ray results, we have realized that the water ligand forms intermolecular hydrogen bonds (O(19)−H(20) = 0.91 Å; O(19)−O(4)^i = 2.733(3) Å; H(20)−O(4)^i = 1.86 Å, O(19)−H(20)−O(4)^i = 161°; symmetry operation: (*i*) = *x*, 0.5 − *y*, *z*) with the peroxo groups of two adjacent complexes in the crystal. Since our calculations were performed for the isolated complex, these intermolecular interactions were not taken into account. As a result, a spurious and strong intramolecular interaction between the hydrogen atoms of water and the peroxo group is favored (see Table 2), whose illustration is given in the Supporting Information. Such an intramolecular interactions of the hydrogen atoms toward the peroxo group cause a displacement of the oxygen atom in the water ligand leading to a very long bond distance between the Mo ion and the O(19) atom. Therefore, we have included in our simulation two methanol molecules that would form hydrogen bonds with the water ligand, and its optimized structure is presented in Figure 2. With this simulation we have intended not only to mimic the intermolecular hydrogen bonds in the crystal packing, but also the solvent effects when the crystal is dissolved into alcoholic solution, because it is believed that the compound $MoO(O_2)_2(OPy)(H_2O)$ retains its solid-state structure in solution. The calculated results for the molecular structure of the complex in the presence of the two methanol molecules are also listed in Table 2 where column **I** refers to calculated values for $MoO(O_2)_2(OPy)(H_2O)$ compound, while column **II** corresponds to the $MoO(O_2)_2(OPy)(H_2O)-(CH_3OH)_2$ system.

An analysis of the results shows a significant decrease in the Mo−O(19) bond distance from 2.811 to 2.330 Å. In addition, the spurious intramolecular interactions between the hydrogen atoms of the water and the peroxo oxygen atoms disappear. There are two intermolecular hydrogen bonding between water ligand and the two methanol molecules (see Table 2 and Figure 2). These interactions cause a decrease of the Mo-centered bond angles between the oxo and peroxo oxygen atoms (O(1)MoO(x), with $x = 3$, 4, 5, or 6) and a concomitant increase of the O(3)MoO(5) bond angle. The absolute error decreased from 0.167 to 0.048 Å for the calculated bond distances and from 5.3° to 1.7° for the calculated bond angles. The errors for some calculated geometrical parameters are shown in the Table 3.

---

(33) Gisdakis, P.; Antonczak, S.; Köstlmeier, S.; Herrmann, W. A.; Rösch, N. *Angew. Chem., Int. Ed..* **1998**, *37*, 2211.

(34) Di Valentin, C.; Gisdakis, P.; Yudanov, I. V.; Rösch, N. *J. Org. Chem.* **2000**, *65*, 2996.

(35) Deubel, D. V.; Sundermeyer, J.; Frenking, G. *Inorg. Chem.* **2000**, *39*, 2314.

(36) Hroch, A.; Gemmecker, G.; Thiel, W. R. *Eur. J. Inorg. Chem.* **2000**, *5*, 1107.

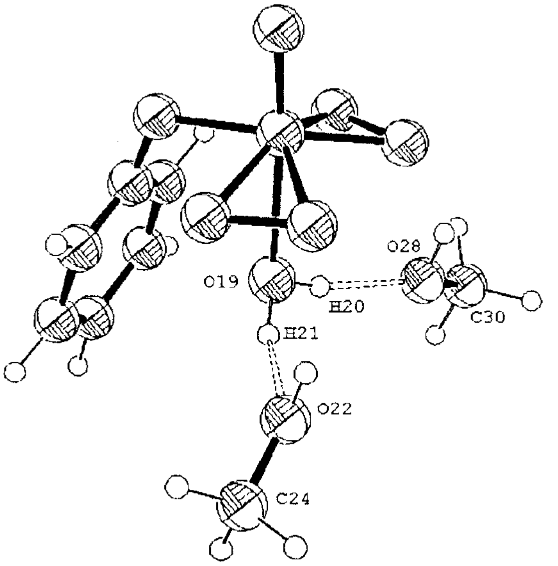

Figure 2. The calculated molecular structure of the $MoO(O_2)_2(OPy)(H_2O)$ with two methanol molecules simulating intermolecular hydrogen bonds.

Table 3. Unsigned Absolute Errors for Selected Bond Distances and Angles for $MoO(O_2)_2(OPy)(H_2O)$ (**I**) and $MoO(O_2)_2(OPy)(H_2O)-(CH_3OH)_2$ (**II**)

error average	I	II
all bond distances (Å)	0.167	0.048
bond distances[a] (Å)	0.021	0.023
bond distances[b] (Å)	0.430	0.093
bond angles (deg)	5.3	1.7
dihedral angles (deg)	3.8	1.2

[a] Excluding the bond distance associated with the water ligand. [b] Taken into account only the bond distances related to water ligand.

The explicit consideration of the intermolecular interactions by the two methanol molecules reconcile the theoretical results with the experimental ones. However, it should be mentioned that, in fact, the potential energy surface is very flat along the stretching of the Mo−O(19), as has been pointed out earlier by Rosch[34] for a related complex. For instance, performing a relaxed potential energy surface scan, with complete geometry optimization at each point, of the Mo−O(19) bond distance ranging from 2.30 to 2.60 Å, yielded energy differences smaller than 1.0 kcal/mol. This is an important result, because in addition to showing the reliability of these ab initio calculations when the structures are properly simulated, it also shows that the presence of the hydrogen bonds between the water ligand and the two methanol molecules greatly decreases the bond distance between this water and the Mo ion. It should then be expected that the dissociation of this water ligand would be hindered in hydrogen bonding solvents. This result might has implication in the reactivity of this compound since the catalytic routes involve, as a first step, the loss of the water ligand.[2,37] The observed hydrogen bonds is then believed to be, in some extent, the reason for the seven-coordinated diperoxo molybdenum complexes being much less reactive toward epoxidation of olefins than the six-coordinated ones. Our results also suggest that this oxidation reaction should be favored in a non-hydrogen bonding solvent and that the inclusion of specific interactions with the solvent is mandatory in order to obtain realistic molecular modeling results. In fact, the metal-mediated epoxidation of olefin mechanism has been subjected to a great deal of experimental and theoretical studies. Two main mechanisms concerning stoichiometric olefin epoxidation by $MoO(O_2)_2(L_1,L_2)$ have generated a long controversy, namely, Mimoun[2] proposed a coordination of the olefin at the metal and a subsequent cycloinsertion into a metal-peroxo bond forming a five-membered dioxymetallocycle that decomposes into an epoxide and the corresponding monoperoxo complex, while Sharpless et al.[37] suggested an alternative mechanism involving the transfer of one of the peroxo oxygens to the olefin through a three-membered ring transition state. Recently, two theoretical studies have corroborated the mechanism suggested by Sharpless.[34,38]

4. Conclusions

The X-ray crystallographic structure of the oxo-diperoxo $MoO(O_2)_2(OPy)(H_2O)$ complex reveals the formation of intermolecular hydrogen bonds between the water ligand and the peroxo groups of adjacent complexes in the crystal. The DFT-B3LYP calculations yielded results for the molecular structure of the isolated complex that are in good agreement with the experimental data, except for the $Mo-OH_2$ bond distance. The presence of these intermolecular hydrogen bonds observed in the X-ray analysis were considered via inclusion of two methanol molecules, and a good agreement between theoretical and experimental results is then obtained, mainly for the geometrical parameters associated with the water ligand. This shows the importance of using ab initio methods in conjunction with a model system that mimics the important interactions present in the real system. In addition, solvent effects has been inferred from the shortening, and consequently, the strengthening, of the Mo−water bond when this complex is dissolved in hydrogen bonding solvents. Therefore, the present results suggest that for rationalization of the molecular mechanism associated with the oxidation reaction it is important to take into account the presence of discrete solvent molecules that form hydrogen bonds with the water ligand.

Acknowledgment. This work was supported by Brazilian funding agencies: FAPESP/CEPID, CAPES, CNPq/PRONEX, and the “Programa de Colaboracíon Científica con Iberoamérica” supported by the Ministerio de Educación y Cultura del Gobierno Español; Proyeto: 8i051. The authors wish also to thank the computer centers NAR-UFSCar, CENAPAD-SP, CESUP-RS (Brazil), and Servei d’Informàtica de la Universitat Jaume I-Castellon-Spain for making their computational facilities available.

Supporting Information Available: A Crystallographic Information File (CIF) format is provided as well as figures containing the intermolecular hydrogen bonding network and containing the DFT-B3LYP calculated molecular structure of the isolated $MoO(O_2)_2(OPy)(H_2O)$ compound. This material is available free of charge via the Internet at http://pubs.acs.org.

IC010020H

---

(37) Sharpless, K. B.; Townsend, J. M.; Williams, D. R. *J. Am. Chem. Soc.* **1972**, *94*, 295.

(38) Deubel, D. V.; Sundermeyer, J.; Frenking, G. *J. Am. Chem. Soc.* **2000**, *122*, 10101.