Molecular oxygen activation by a molybdenum(IV) monooxo bis(β-ketiminato) complex†

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Received (in Cambridge, UK) 24th November 2006, Accepted 18th December 2006
First published as an Advance Article on the web 9th January 2007
DOI: 10.1039/b617199k

Molybdenum(IV) monooxo compound that contains bis(β-ketiminato) ligands activates molecular oxygen forming a molybdenum(VI) monooxo peroxo compound, representing a new entry into molybdenum peroxo derivatives.

Dioxygen is a readily available, clean oxidant and is increasingly being favored in green chemistry. However, its reactivity makes control of the reaction products a challenge. A series of metalloenzymes catalyze specific oxidations with oxygen; they include oxidases, peroxidases, monooxygenases and dioxygenases. Most of them contain heme or nonheme iron, and/or copper centers.[1] In contrast, a group of enzymes also transfers an oxygen atom to or from a substrate but water acts as the source of oxygen rather than dioxygen. These enzymes are referred to as oxotransferases in the case of a primary oxygen atom transfer or hydroxylases when water is directly involved.[2] They contain molybdenum or tungsten in their active sites. For this reason many Mo and W oxo compounds have been prepared and their oxygen atom transfer capability investigated.[3] In addition, molybdenum complexes with the *cis*-$[MoO_2]^{2+}$ core have found wide application in industrial reactions due to their oxidation properties.[4]

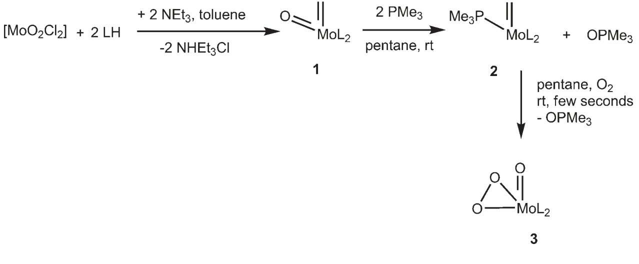
In this context, it is of interest to examine the reactivity of dioxygen on the one hand towards molybdenum and on the other hand towards iron or copper complexes in the hope of understanding the preference for molybdenum in oxotransferases and providing fresh insight for the design of chemical catalysis. The reaction of iron and copper complexes with dioxygen has been intensively studied and several peroxo species have been characterized by various means.[5] However, the reaction of molybdenum complexes with dioxygen has been far less of a subject of investigation and the isolation of a peroxo species from such a reaction is extremely rare.[6,7] Presumably for this reason, in the few examples of molybdenum catalyzed oxidations involving dioxygen, authors do not assume peroxo intermediates.[8]

We have recently reported trigonal prismatic molybdenum dioxo complexes that contain η²-pyrazolate ligands and that are capable of transferring an oxygen atom from DMSO to triphenylphosphine.[9,10] The unusual coordination geometry is relevant to the structure of DMSO reductase.[11] Our ongoing interest in oxygen atom transfer catalysis has led us to explore molybdenum dioxo complexes that contain β-ketiminato ligands derived from acetylacetone together with their oxygen atom transfer capability as well as their reactivity towards dioxygen. Here, we report the peroxo product of the latter reaction that is fully characterized by spectroscopic as well as crystallographic means and represents a rarely reported example of this type of reactivity.[6,7]

Treatment of $[MoO_2Cl_2]$[12] with two equivalents of 4-(2,6-dimethyl-phenylimino)-pent-2-en-ol[13] (LH) in the presence of excess triethylamine in toluene at −20 °C for 4 hours at room temperature gives $[MoO_2L_2]$ (**1**) in moderate yield (Scheme 1). Usual work-up gives bright yellow **1** that can be purified by washing with cold pentane and recrystallization from toluene at −20 °C.

Oxygen atom transfer properties of **1** to trimethylphosphine were investigated. A solution of **1** was treated with a five-fold excess of PMe_3 in benzene-d_6 at room temperature and the reaction was monitored by ^{31}P NMR spectroscopy. The first spectrum taken 2 minutes after addition of the phosphine shows a resonance for PMe_3 and two new resonances of equal intensity at −5.7 ppm and 31.0 ppm. The latter belongs to the phosphorus atom of $OPMe_3$, whereas the former is assignable to the trimethylphosphine adduct $[MoOL_2(PMe_3)]$ (**2**) (*vide infra*). Monitoring of the reaction revealed complete conversion to **2** after 2 hours. Unambiguous evidence for the nature of **2** was given by its isolation and independent characterization. Thus, addition of PMe_3 to a yellow pentane suspension of **1** leads after 2 hours to a green clear solution, from which **2** can be isolated at −80 °C as green needles in moderate yield. Spectroscopic data confirm the formation of the diamagnetic adduct.

The stoichiometric oxygen atom transfer (OAT) from **1** to trimethylphosphine was additionally monitored by UV/Vis spectroscopy as shown in Figs. 1A, 1B. The reaction was performed with a 50-fold excess of trimethylphosphine over molybdenum complex **1**. UV/Vis spectra were recorded every three minutes between 280 and 500 nm. Two processes are involved, as indicated by a first set of spectra leading to two clean isosbestic



Scheme 1 Formation of compounds **1**, **2** and **3**.

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† Electronic supplementary information (ESI) available: Experimental details. See DOI: 10.1039/b617199k

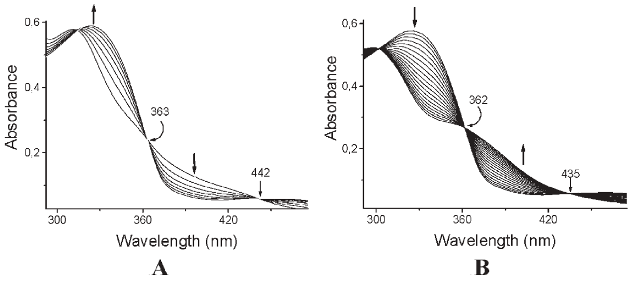

Fig. 1 (A) Reduction of **1** in toluene at rt. Spectra recorded from $t = 3$ to 21 minutes. (B) Reduction of **1** in toluene at rt. Spectra recorded from $t = 40$ to 100 minutes.

points at 363 and 442 nm (Fig. 1A) and a second set of spectra with isosbestic points at 362 and 435 nm (Fig. 1B). The first process is significantly faster than the second one so that the absorption at *e.g.* 339 nm *vs.* time reaches a maximum after 27 minutes with a slow decrease in the following 40 minutes. The absorbance difference (AD) diagrams showed non-linear curves and the absorbance difference quotient (ADQ) diagrams showed straight lines (see Supporting Information). These two diagrams are in accordance with the Mauser diagrams for two independent consecutive reactions.[14] Thus, it is highly likely that the reaction taking place here is consecutive of the type A → B → C. Detailed kinetic data are currently being investigated and will be published in due course.

The UV/Vis spectrum of an isolated sample of **2** is consistent with the one after completion of the second process. Therefore, we assume that initially the phosphine reacts with one of the two oxo groups forming a compound with a coordinated phosphine oxide ligand [$MoOL_2(OPMe_3)$], whereas the second process corresponds to the substitution of the phosphine oxide by PMe_3 forming **2**. Although it is generally accepted that OAT reactions consist of two transition steps, investigated systems have rarely allowed the study of both processes in a separate way. Only very recently, the isolation of the intermediate molybdenum compound with a coordinated phosphine oxide ligand has been reported.[15] Determination of bond dissociation energies indicates that the formation of the intermediate represents the driving force for the OAT reaction. This is consistent with the results reported here, where formation of the intermediate phosphine oxide adduct is faster relative to the subsequent substitution reaction with phosphine. Interestingly, the highly dilute conditions for UV/Vis spectroscopy favor the formation of the phosphine oxide adduct and decrease the rate of the substitution reaction whereas the more concentrated NMR conditions lead to fast substitution of coordinated $OPMe_3$ forming **2** as the ^{31}P NMR spectra show no evidence for a compound with coordinated phosphine oxide (*vide supra*).

The catalytic oxygen atom transfer from dimethylsulfoxide (DMSO) to PMe_3 with 5 mol% of **1** at room temperature was monitored by ^{31}P NMR spectroscopy. After 2 hours the phosphine was fully oxidized. The constant yellow color of the reaction throughout the transfer indicates that no μ-oxo compound of the type [$L_2MoO(\mu\text{-}O)OMoL_2$] is formed as such Mo(V) compounds usually show purple colors.[16]

The reactivity of **2** towards dioxygen was investigated. After exposing green toluene or pentane solutions of **2** to dry molecular oxygen for few seconds, a quick color change from green to red–orange occurred. From such solutions orange crystals can be isolated, that proved to be the monooxo peroxo complex [$MoO(O_2)L_2$] (**3**) as shown in Scheme 1. The ^1H NMR spectrum of **3** in benzene-d_6 shows eight resonances of equal intensity for protons of methyl groups pointing to two non-equivalent coordinated ligands, which is confirmed by X-ray diffraction analysis (*vide infra*). In the IR spectrum the ν(O–O) vibration appears at 864 cm^{-1} as a weak intensity band corresponding to the data described in the literature.[17,18]

Compound **3** represents the product of activation of molecular oxygen. This kind of activation is extremely rare in molybdenum chemistry.[6,7] To the best of our knowledge only two systems have been reported: [$MoO(CN)_5$][PPh_4]$_3$ and porphyrin Mo^{IV}=O compounds were shown to react with O_2 forming corresponding oxo peroxo compounds.[6,7] The rareness of reports for this type of reaction is surprising as the type of compound formed (monooxo peroxo) is relatively abundant.[17,18] However, the typical method for the synthesis of compounds of the type [$MoO(O_2)L_2$] or [$MoO(O_2)_2L$] starts from MoO_3 by reaction with the appropriate ligand in aqueous H_2O_2 media. This method of preparation is not applicable to the ligand system reported here as the final product is sensitive to hydrolysis. This renders the reaction described here to be a new method for preparing monooxo peroxo complexes that are sensitive to water or to hydrogen peroxide (*e.g.* in the ligand backbone).

Fig. 2 shows the molecular structure of [$MoO(O_2)L_2$] (**3**) determined by X-ray diffraction analysis‡ along with selected bond lengths and angles. The molybdenum atom is heptacoordinated by an oxo, a η^2-peroxo and two bidentate L ligands presenting a distorted pentagonal bipyramid (largest angle: O1–Mo1–O5 = 168.4(1)°). The axial sites are occupied by the oxo group O1 and O5 (oxygen atom of one of the two ligands L). The other ketiminato oxygen atom O4, two amido nitrogen atoms (N1, N2) being *trans* to each other, and the η^2-peroxo moiety (O2, O3) define the equatorial plane. The bond distances and angles correspond to those of other heptacoordinate molybdenum oxo peroxo compounds described in the literature.[6,17,18]

In summary, the molybdenum dioxo bis(β-ketiminato) complex can be conveniently reduced to the corresponding Mo(IV)

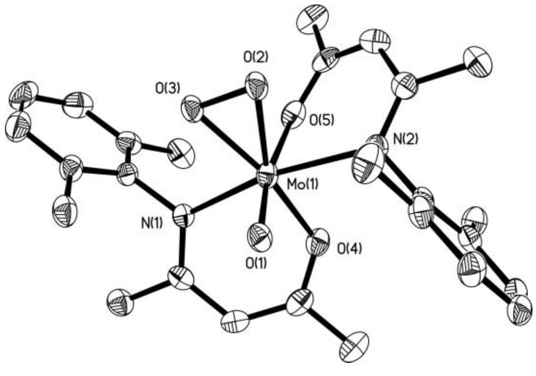

Fig. 2 Molecular structure of **3** (ORTEP with 50% probability). Selected bond lengths [Å] and angles [°]: Mo1–O1 1.673(2), Mo1–O3 1.936(2), Mo1–O2 1.951(2), Mo1–O4 2.044(2), Mo1–O5 2.094(2), Mo1–N1 2.184(2), Mo1–N2 2.198(2), N1–Mo1–N2 160.9(1), O1–Mo1–O3 104.0(1), O4–Mo1–N1 80.9(1), O3–Mo1–O4 154.3(1), O3–Mo1–O2 43.5(1).

monooxo complex by oxygen atom transfer reaction to trimethylphosphine. The reduced compound is capable of rapid activation of molecular oxygen forming a monooxo peroxo complex. This is a rare example of this type of reaction and represents a potentially new method for preparing monooxo peroxo compounds that are prone to hydrolysis. Furthermore, in mechanisms of molybdenum catalyzed oxidations the formation of intermediate peroxo species needs to be considered. Current research is focused on the investigation of the reactivity of the peroxo compound **3** in various oxygen atom transfer reactions of stoichiometric and catalytic nature.

Support of this work by a grant of the Deutsche Forschungsgemeinschaft (MO 963/2) is gratefully acknowledged.

Notes and references

‡ Crystal data for **3**: $C_{26}H_{32}MoN_2O_5 \cdot 1.5\ C_7H_8$, M_w = 686.68, triclinic, space group $P\bar{1}$, a = 11.700(2), b = 12.012(2), c = 12.815(2) Å, α = 77.95(3)°, β = 73.18(3)°, γ = 78.95(3)°, V = 1669.3(5) $Å^3$, Z = 2, ρ_{calc} = 1.366 Mg m^{-3}, $F(000)$ = 718, λ = 1.54178 Å, T = 100(2) K, $\mu(Cu_{K\alpha})$ = 3.567 mm^{-1}. Data for the structure were collected on a Bruker three-circle diffractometer equipped with a Smart 6000 CCD area detector using mirror-monochromated $Cu_{K\alpha}$ radiation. The structure was solved by direct methods using SHELXS-97[19] and refined against F^2 on all data by full-matrix least-squares with SHELXL-97.[19] All non-hydrogen atoms were refined anisotropically, while all hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model with U_{ij} tied to the parent atom. Only the hydrogen bonds to C3 and C8 were not included on calculated positions but found in the electron density map and then refined with distance restraints, because they were not lying exactly in the plane of the carbon atoms. Intensity measurements were performed on a rapidly cooled crystal in the range $3.65 \leqslant \theta \leqslant 58.75$. Of the 11416 measured reflections 4347 were independent (R_{int} = 0.0319). The oxo and the peroxo group were disordered. For *ca.* 10% of the crystal the oxo group is lying on the position of the peroxo group and *vice versa*. A toluene molecule lying on the inversion center and a further toluene molecule were also disordered. All disordered groups were refined with distant restraints and restraints for the anisotropic displacement parameters. The final refinements converged at $R1 = 0.0256$ for $I > 2\sigma(I)$, $wR2 = 0.0673$ for all data. The final difference Fourier synthesis gave a min./max. residual electron density −0.374/+0.361 e $Å^3$. CCDC 618904. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b617199k

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