Available online at www.sciencedirect.com

ScienceDirect

Inorganica Chimica Acta 359 (2006) 4407–4411

Inorganica Chimica Acta

www.elsevier.com/locate/ica

Note

Hydrogen bonding interaction between imidazolyl N–H group and peroxide: Stabilization of Mn(III)-peroxo complex $Tp^{iPr2}Mn(\eta^2\text{-}O_2)(im^{Me}H)$ ($im^{Me}H$ = 2-methylimidazole) ☆

Udai P. Singh [a,*], Asish K. Sharma [a], Shiro Hikichi [b,*], Hidehito Komatsuzaki [b], Yoshihiko Moro-oka [b], Munetaka Akita [b]

[a] *Department of Chemistry, Indian Institute of Technology Roorkee, Roorkee 247 667, India*
[b] *Chemical Resources Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan*

Received 19 February 2006; received in revised form 18 June 2006; accepted 21 June 2006
Available online 27 June 2006

Abstract

A mononuclear side-on peroxo managanese (III) complex, $Tp^{iPr2}Mn(\eta^2\text{-}O_2)(im^{Me}H)$ (**3**) was prepared by the reaction of $[Tp^{iPr2}Mn(O)]_2$ with excess amount of H_2O_2 in the presence of 2-methylimidazole ($im^{Me}H$). Its X-ray structure clearly demonstrated the involvement of intermolecular hydrogen bonding interaction between η^2-peroxide and imidazolyl N–H functional group. Complex **3** was stable, green in color and unable to oxygenate triphenylphosphine and ethyl vinyl ether.

Keywords: Manganese(III); Peroxo complex; Crystal structure; 2-Methylimidazole

1. Introduction

Hydrogen bonding is very important chemical interactions and in nature the biological system uses such type of a non-covalent interactions very frequently for molecular recognition, proton transfer, structural stabilization, and so on. In the dioxygen metabolic processes mediated by metalloproteins, hydrogen bonding interaction between the protic hydrogen and the metal bonded dioxygen molecule play important roles for the stabilization of the metal-oxygen species and O_2 activation. For instance, an imidazole of the "distal" histidine residue interacts with the iron-coordinated O_2 molecule in oxy-hemoglobin/myoglobin [1,2]. In order to get the comprehensive insight into metal-dioxygen chemistry, our groups are extensively involved in study the dioxygen complexes of various first- and second-row transition metals with hydrotris(pyrazolyl)borate ligands (=Tp^R) as tridentate ligand [3]. Manganese-dioxygen complexes are attractive targets for us as such species ($Mn–O_2^-, O_2^{2-}$, OOH^- and O^{2-}) are suggested to play an important role as key intermediates in the physiological dioxygen metabolism and in oxidation of various organic substrates [4–8]. In our previous work of the side-on peroxo complex having the neutral pyrazole ligand, $Tp^{iPr2}Mn^{III}(\eta^2\text{-}O_2)(pz^{iPr2}H)$ (**1**), X-ray structures of both isomers of **1** showed that one isomer involved the intramolecular hydrogen-bonding interaction between the η^2-peroxide and the N–H functional group of the pyrazole ligand [9]. But the interaction between $pz^{iPr2}H$ and Mn in **1** was not so strong, and the role of the pyrazole ligand was not very clear. Herein we report unique structural properties of a novel Mn(III)-η^2-peroxo complex to demonstrate the stabilization effect of the hydrogen-bonding interaction between imidazolyl N–H functional group and $M–O_2$ framework.

☆ Abbreviations used in this paper: $Pz^{iPr2}H$ = 3,5-diisopropylpyrazole; $Tp^{iPr}2$ = hydrotris(3,5-diisopropyl-1-pyrazolyl)borate or $HB(3,5\text{-}iPr_2pz)_3^-$ $im^{Me}H$ = 2-methylimidazole.

* Corresponding authors. Tel.: +91 1332 285329; fax: +91 1332 273560 (U.P. Singh).
E-mail address: udaipfcy@yahoo.co.in (U.P. Singh).

0020-1693/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.ica.2006.06.033

2. Experimental

2.1. Instrumentation

Carbon, hydrogen, and nitrogen were analyzed with a Vario EL III elemental analyzer. IR spectra were recorded as KBr pellets on Thermo Nicolet (Nexus FT-IR). Electronic spectral measurement was carried out on a Perkin–Elmer Lambda 35 UV/Vis spectrophotometer. The crystal suitable for X-ray measurements was mounted on glass fibres. All measurements were made on a Rigaku RAXIS RAPID imaging plate area detector diffractometer with graphite monochromated detector with Mo Kα radiations ($\lambda = 0.7107$ Å).

2.2. Materials and methods

All solvent used were purified by the literature methods [10]. The highest grade commercially available reagents were used without further purification. All manipulations were performed under argon by standard Schlenk techniques. The complex [(Tp^{iPr2}Mn)(O)]$_2$ was prepared by the methods described earlier [11].

*2.3. Synthesis of Tp^{iPr2}Mn(η^2-O$_2$)(im^{Me}H) (**3**)*

To a solution of [(Tp^{iPr2}Mn)(O)]$_2$ (0.2001 g, 0.1872 mmol) and 2-methylimidazole (0.0306 g, 0.37 mmol) in 15 ml CH_2Cl_2, was added an excess amount of aq. H_2O_2 (35 wt%, 153.50 μl, 1.790 mmol) at room temperature. The solution was vigorously stirred for 15 min and immediately cooled at −70 °C, resulting the green color solution. The excess of H_2O_2 was removed by filtration and the green color filtrate was evaporated to dryness under vacuum. The recrystallization of resultant solid from acetonitrile at −30 °C gave green crystals (0.0712 g, 0.1091 mmol, 60% yield). The elemental analysis was done on a carefully dried sample. *Anal.* Calc. for $C_{31}H_{52}N_8O_2BMn$: C, 58.68; H, 8.26; N, 17.66. Found: C, 57.97; H, 8.48; N, 16.86%. IR (KBr pellet, ν/cm^{-1}): (BH) 2538, (OO) 896. UV–Vis (CH_2Cl_2, nm): 381 (314), 478 (173).

2.4. X-ray data collection and structural determination

Single crystals of **3** · 0.25MeCN were obtained by crystallization from the green acetonitrile solution and mounted on a glass fiber. Diffraction measurement was carried at 15 ± 1 °C. A total of 20 oscillation images were collected. A sweep of data was done using $\acute{\omega}$ oscillations from 28.0° to 118.0° in 4.5° steps. The exposure rate was 798.0 (s/o). The crystal-to-detector distance was 110.00 mm. A total of 15558 reflections were collected of which 13944 were of $I > 2\sigma(I)$ and were used in the final refinement. Readout was performed in the 0.000 mm pixel mode. A summary of the cell parameter, data collection conditions and refinement results is provided in Table 1.

Table 1
Crystal data and data collection details of complex **3** · 0.25 MeCN

Empirical formula	$C_{63}H_{107}B_2N_{16.50}Mn_2O_4$
Formula weight	1291.14
Crystal system	monoclinic
Lattice type	primitive
Space group	$P2_1/a$ (#14)
Lattice parameters	
a (Å)	17.680(3)
b (Å)	21.155(7)
c (Å)	20.366(3)
β (°)	100.20(1)
V (Å^3)	7496(3)
Z value	4
D_{calc} (g/cm^3)	1.144
μ (Mo Kα) (cm^{-1})	3.89
Diffractometer	Rigaku RAXIS-IV
Radiation	Mo Kα ($\lambda = 0.71070$ Å) graphite monochromated
Detector aperture	300 mm × 300 mm
Data images	20 exposures
ω Oscillation range	28.0–118.0°
Exposure rate (s/°)	798.0
$2\theta_{max}$ (°)	55.1
Total number of reflections measured	15558
Number of reflections observed	13944
Number of variables	796
Reflection/parameter ratio	17.52
Residuals: R (all reflections)	0.275
Residuals: R_1 ($I > 2\sigma(I)$)	0.099
Residuals: wR_2 (all reflections)	0.252
Goodness of fit indicator	0.991
Maximum shift/error in final cycle	0.013
Maximum peak in final difference map (e$^-$/Å^3)	0.53
Minimum peak in final difference map (e$^-$/Å^3)	−0.47

The structure of the complex was solved by an expanded using Fourier techniques (DIRDIF99) [12]. Some non-hydrogen atoms were refined anisotropically, while the rest were refined isotropically. Hydrogen atoms were refined using the rigid model. Neutral atom scattering factors were taken from Cromer and Waber [13].

3. Results and discussion

For d^0 early transition metal complexes, dehydrative condensation between the oxo complexes and H_2O_2 is one of the very common methods for preparation of peroxo complexes [14]. The same procedure was applied for the preparation of present Mn(III) peroxo complex and the reaction of Mn(III) bis(μ-oxo) complex **2** [11] and H_2O_2 in the presence of 2-methylimidazole (=im^{Me}H) yielded a bluish green complex **3**. On the basis of its bluish green color, and the appearance of ν(O–O) vibration at 896 cm^{-1} in IR spectrum of the complex, **3** was assumed to be the desired Mn(III)-peroxo complex with the imidazole bonded ligand. Single crystals of **3** suitable for X-ray data collection were obtained by crystallization from acetonitrile at −30 °C. The crystallographic data are listed in Table 1 whereas the bond lengths and bond angles are