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Communication

A novel manganese(III)-peroxo complex bearing a proline-derived pentadentate aminobenzimidazole ligand

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Graphical asbtract



• UV-Vis • CSI-TOF MS • CW-EPR

A novel nonheme manganese(III)-peroxo complex bearing a proline-derived pentadentate aminobenzimidazole ligand was synthesized and spectroscopically characterized, and its reactivity in aldehyde deformylation was investigated.

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ABSTRACT

Manganese(III)-peroxo complexes are invoked as key intermediates in the enzymatic cycles of Mn-containing enzymes, and the synthesis of reactive manganese(III)-peroxo complexes with rationally designed ligand has been of great interest in the communities of bioinorganic and biomimetic chemistry. Herein, we designed a novel pentadentate aminobenzimidazole ligand and obtained its manganese(II) complex, which was successfully applied in the synthesis of a reactive manganese(III)-peroxo complex by treatment with hydrogen peroxide in the presence of triethylamine. The manganese(III)-peroxo complex was well characterized with various spectroscopic techniques, including ultraviolet–visible (UV-vis) spectrophotometry, coldspray ionization time-of-flight mass spectrometry (CSI-TOF MS), and continuous wave electron paramagnetic resonance (CW-EPR) spectroscopy. Besides, its reactivity in aldehyde deformylation was investigated, demonstrating second-order kinetics in the reaction with 2-phenylpropionaldehyde and affording acetophenone as the sole product.

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Keywords: Enzyme models Manganese Manganese(III)-peroxo complex Aldehyde deformylation Kinetics

Manganese(III)-peroxo complexes have been suggested as key intermediates in the enzymatic cycles of Mn-containing enzymes, such as manganese superoxide dismutase (MnSOD) [1], catalase [2], and the oxygen-evolving complex (OEC) of photosystem II [3]. In biomimetic studies, a variety of rationally designed heme and nonheme ligands have been applied in the synthesis of reactive manganese(III)-peroxo complexes [4-9]. A notable example of the supporting ligands is the heme ligand TPP (TPP = tetraphenylporphyrin dianion), with which Valentine and co-workers obtained the first X-ray crystal structure of the manganese(III)-peroxo complexes [10]. For nonheme systems, based on the facially-coordinating trispyrazolyl ligand Tp^{iPr2} (Tp^{iPr2} = hydridotris(3,5-diisopropylpyrazolyl)borate anion), two more manganese(III)-peroxo complexes were synthesized and structurally characterized by Moro-oka and co-workers[11,12]. The nonheme macrocyclic TMC (TMC = *N*-tetramethylated cyclam) ligand series is versatile in the chemistry of metal-oxygen adducts, and several structurally characterized and highly reactive manganese(III)-peroxo complexes of TMC have been developed by Nam and co-workers [13-15].

The nonheme amino *N*-heteroarene ligands, such as aminopyridine, aminoquinoline and aminoimidazole ligand, have also been extensively investigated in the synthesis of manganese(III)-peroxo complexes (see Fig. 1 for selected examples of aminopyridine ligand N4Py, aminoquinoline ligand L^7q_2 , and aminoimidazole ligand im L_5^2) [16-25]. On the other hand, the aminobenzimidazole ligand series, another member of the nonheme amino *N*-heteroarene ligand family, has been frequently used in the metal complex-catalyzed oxidation of organic substrates [26-35]. Recently, our group has succeeded in highly efficient (enantioselective) oxidation of hydrocarbons, olefins and alcohols with aqueous H_2O_2 as a terminal oxidant under mild conditions, in which the proline- derived aminobenzimidazole ligands play key roles in modulating the catalytic reactivity of the manganese complexes [26,36-39].

On the basis of these above work, we are interested in the investigation of the activity of manganese(III)-peroxo complex bearing an aminobenzimidazole supporting ligand. Herein, we report the synthesis and characterization of a novel manganese(III)-peroxo complex supported by a proline-derived aminobenzimidazole ligand Pro3Bzim (Fig. 1). The corresponding manganese(III)-peroxo complex is characterized by means of various spectroscopic methods, and its reactivity in aldehyde deformylation is also investigated.

We initiated our study by preparation of the precursor Mn^{II} complex using an aminobenzimidazole ligand Pro3Bzim (Pro3Bzim = (*S*)-*N*,*N*',*N*'-tris(*N*-methylbenzimidazol-2-ylmethyl)-2-pyrrolidinemethanamine), which was readily synthesized from proline-derived diamine skeleton (*S*)-2-pyrrolidinemethanamine and 2-chloromethyl-*N*-methylbenzimidazole by following a modified procedure for the synthesis of its analogue Pro3Py (Pro3Py = (*S*)-*N*,*N*',*N*'-tris(2-picolinyl)-2-pyrrolidinemethanamine) in our previous report [40] (see the Supporting information for ¹H and ¹³C NMR spectra of ligand Pro3Bzim). Reacting Pro3Bzim with equimolar amounts of Mn(OTf)₂ in CH₃CN at ambient temperature afforded the desired [Mn^{II}(Pro3Bzim)(OTf)](OTf) complex (**1**-OTf) (Scheme 1).

Single crystals of 1-OTf were obtained by diffusing ether into the CH_3CN solution. X-ray crystallographic analysis reveals that the Mn^{II} center resides in a distorted octahedral geometry and the Pro3Bzim ligand is coordinated to Mn^{II} ion with five N donor atoms, two from the diamine backbone and three from the benzimidazole moieties. A triflate ligand is bound to the manganese center in the capacious apical position, indicating a labile site for the binding of peroxo ligand (See also Table S1 and S2 in the Supporting information for crystallographic data of 1-OTf).

With the Mn^{II} starting material in hand, we set out to synthesize the corresponding Mn^{III}-peroxo complex by following a conventional protocol [4]. Treating the colorless solution of 1 in CH₃CN with H_2O_2 (40 equiv.) in the presence of triethylamine (5 equiv.) at 20 °C for about 2 min resulted in the completely formation of a pink species (2) with a characteristic ultraviolet-visible (UVvis) absorption band at 540 nm ($\varepsilon = \sim 140$ L mol⁻¹ cm⁻¹, Fig. 3a), which is in agreement with the reported manganese(III)-peroxo complexes [23]. It should be noted that 2 is metastable with a half-life about 0.5 h at 20 °C (see Fig. S3 in the Supporting information for the time profile of the natural decay of 2), and the metastable property has often been regarded as a characteristic feature of the reactive metal-oxygen adducts [41-44]. In order to identify the structure of 2, it was further characterized with coldspray ionization time-of-flight mass spectrometry (CSI-TOF MS) and continuous wave electron paramagnetic resonance (CW-EPR). The CSI-TOF-MS of 2 in positive mode exhibited a dominant ion peak at a mass-to-charge (m/z) ratio of 619.2, whose mass and isotope distribution pattern correspond to $[Mn^{II}(Pro3Bzim)(O_2)]^+$ (calculated m/z 619.2) (Fig. 3 b). When 2 was prepared with isotopically labeled H₂¹⁸O₂ in the presence of triethylamine, a dominant ion peak corresponding to $[Mn^{III}(Pro3Bzim)({}^{18}O_2)]^+$ appeared at m/z 623.2 (calculated m/z623.2) (Fig. 3b, inset). The mass shift of 4 Daltons confirms that species 2 contains an O_2 moiety in the coordination sphere. The Xband CW-EPR spectrum of a frozen solution of 2 appears silent, as expected for the Mn^{III} oxidation state, which is in accordance with the manganese(III)-peroxo complexes in literature [13,14]. Based on the spectroscopic characterizations above, the new species 2 proves to be a manganese(III)-peroxo complex, assigned as $[Mn^{III}(Pro3Bzim)(O_2)]^+$. Given that the structure of ligand Pro3Bzim is similar to Pro3Py, taken together, it is likely that 2 possesses a similar coordination geometry to $[Mn^{III}(Pro3Py)(O_2)]^+$ and the peroxo moiety is bound side-on as deduced for the latter and some other manganese(III)-peroxo complexes [6,40].

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Aldehyde deformylation is frequently used as a probe reaction to evaluate the reactivity of metal-peroxo complexes [4,40,45-50]. Therefore, we were inspired to examine the kinetic reactivity of **2** by using 2-phenylpropionaldehyde (2-PPA) as a probe substrate with UV-vis spectrophotometry. Upon addition of 2-PPA to **2** in CH₃CN at 20 °C, the absorption band at 540 nm, the typical absorption of manganese(III)-peroxo **2**, decreased with a pseudo-first-order kinetics profile (Fig. 4a). GC-MS analysis of the resulting solution revealed the formation of acetophenone as the sole product, as observed in the deformylation of 2-PPA by other metal-peroxo complexes [15,40,45-49]. The first-order rate constant (k_{obs}), determined by pseudo-first-order fitting of the kinetic data for the decay of **2** monitored at 540 nm, increased linearly with increasing concentration of 2-PPA, thereby giving a second-order rate constant (k_{2}) of 0.10 L mol⁻¹ s⁻¹ at 20 °C (Fig. 4b). This reaction rate is comparable with the reported manganese(III) -peroxo complexes [15,40,50]. Thus, we demonstrate that **2** is capable of performing oxidative deformylation reaction of aldehyde with second-order kinetics.

In summary, we have employed a proline-derived pentadentate aminobenzimidazole ligand (Pro3Bzim) to synthesize the N5-Mn^{II} complex (1), which was crystallographically characterized and further used in the preparation of a novel manganese(III)-peroxo complex (2) by a conventional protocol with H_2O_2 in the presence of triethylamine. The structure of 2 was well characterized with various spectroscopic techniques, including UV-vis, CSI-TOF MS and CW-EPR, while the reactivity of 2 was investigated in oxidative deformylation of aldehyde, demonstrating second-order kinetics in the reaction with 2-phenylpropionaldehyde and affording acetophenone as the sole product. The aminobenzimidazole ligands have proven to be excellent candidates in the development of enzyme models toward to catalytic oxidation reactions. The present work provides valuable example for this type ligands in the study of synthetic metal-oxygen adducts. Further investigations focusing on the development of more effective and versatile amino *N*-heteroarene ligands are underway in our lab.

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Fig. 1. Selected examples of nonheme amino N-heteroarene ligands for manganese(III)-peroxo complexes.



Fig. 2. ORTEP plot for [Mn^{II}(Pro3Bzim)(OTf)]⁺ (1; CCDC-1832630) with 50% probability thermal ellipsoids and H atoms omitted for clarity. Atom colors: Mn, violet; C, gray; N, blue; O, red; F, green; S, yellow.



Fig. 3. Spectroscopic characterizations of **2**: (a) The changes of UV-vis absorption spectra showing the formation of **2** (red line) observed in the oxidation of **1** (1 mmol/L, blue line) by H_2O_2 (40 mM) in the presence of triethylamine (5 mmol/L) in CH₃CN at 20 °C. Inset shows the time profile monitored at 540 nm for the formation of **2**. (b) CSI-TOF-MS spectrum of **2**. Inset shows the isotope distribution patterns of **2**-¹⁶O (blue line) and **2**-¹⁸O (red line). (c) X-band CW-EPR spectrum of **2** recorded at 5 K.



Fig. 4. Kinetics of the reaction of **2** with 2-PPA: (a) UV-vis absorption spectral changes observed in the reaction of **2** (1 mmol/L, red line) with 2-PPA (90 mmol/L) in CH₃CN at 20 °C. Inset shows the time profile of **2** monitored at 540 nm obeying *pseudo*-first-order kinetics. (b) Plot of the first-order rate constant (k_{obs}) against the concentration of 2-PPA to determine the second-order rate constant (k_2) in the reaction of 2-PPA with **2** (1 mmol/L) in CH₃CN at 20 °C.

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 $\label{eq:scheme 1. Syntheses of precursor complex $[Mn^{II}(Pro3Bzim)(OTf)]^{+}(1)$ and manganese(III)-peroxo complex $[Mn^{III}(Pro3Bzim)(O_2)]^{+}(2)$. }$