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Synthesis, spectroscopic characterization and hydroxylation of Mn(II) complexes with bis(2-pyridylmethyl)benzylamine

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ABSTRACT

Two new Mn(II) complexes of bis(2-pyridylmethyl)benzylamine (bpa) were synthesized and characterized by elemental analyses, IR and UV–visible spectroscopies, thermal analyses and ES-MS. These complexes are stable in air with the formula of $[(pba)_2Mn_2Cl_2(\mu\text{-}Cl)_2]$ (1) and $[(pba)_2Mn_2(H_2O)_2(\mu\text{-}Ac)_2](Ac)_2$ (2). The spectroscopic titration results show that the complexes could react with H_2O_2 resulting active oxidants, which could cause the intramolecular aromatic hydroxylation. The hydroxylated ligand (pba-OH) was confirmed by ES-MS and HPLC.

1. Introduction

Biomimetic oxygenation reactions using the model compounds of non-heme dioxygenases have attracted much attention in the communities of bioinorganic and oxidation chemistry [1,2]. Hydroxylation belongs to the oxygen transfer reactions introducing the hydroxyl group (–OH) into organic molecules, primarily via the substitution of functional groups or hydrogen atoms. Selective hydroxylation of aromatic compounds is among the most challenging chemical reactions in synthetic chemistry and has gained steadily increasing attention during recent years, particularly because of the use of hydroxylated aromatics as precursors for pharmaceuticals [3]. Recently, intramolecular aromatic and aliphatic ligand hydroxylation as well as intermolecular phenolate oxygenation, H-atom abstraction by the models of tyrosinase has been studied extensively in connection with the catalytic mechanism of tyrosinase [4–6].

Manganese complexes bearing non-heme ligands, such as salen- and tacn-derived ligands have shown promise as versatile catalysts in olefin epoxidation and alkane hydroxylation [7–9]. The dinuclear manganese complexes with pyridine and (pyridylmethyl)amine ligands were able to catalyze the oxidation of several alkenes to the corresponding epoxides using H_2O_2 as oxidants [10]. Binuclear manganese(II) complexes $[Mn_2(\mu\text{-}O_2CCH_3)_3L_2]^+$ (L = bis(pyridylmethyl)amine) were studied for their ability to disproportionate hydrogen peroxide [11]. The complex $[Mn_2(\mu\text{-}Cl)_2L_2Cl_2]$ was also synthesized although the ability of this complex to disproportionate hydrogen peroxide was not reported [12]. Up to now the intramolecular hydroxylation catalyzed by the manganese(II) complexes were not reported. Here we report the synthesis, spectroscopic characterization and intramolecular aromatic hydroxylation of Mn(II) complexes with bis(2-pyridylmethyl)benzylamine (bpa).

2. Experimental

2.1. Materials and instrumentation

All reagents are of commercial grade and used as received. IR spectra were recorded on a Nicolet 210 spectrometer in KBr pellets. Elemental analyses were performed by the PerkinElmer 240. The molar electrical conductivities in DMF solution containing 10^{-4} mol L^{-1} complex were measured at 25 ± 0.1 °C using a BSA-A conductmeter. Thermogravimetric analysis was carried out in nitrogen atmosphere with a heating rate of 10 °C min^{-1} using a Shimadzu DT-40 thermal analyzer. ^{1}H NMR and ^{13}C NMR spectra were measured on a Bruker 400 MHz spectrometer. The electronic absorption spectra were recorded in the 900–190 nm region using the UV-2450 spectrophotometer. The electrospray-mass spectral (ES-MS) were determined on a Finnigan LCQ mass spectrograph and the concentration of the samples were about 1.0 μmol L^{-1}. The diluted solution was electrosprayed at a flow rate of 5×10^{-6} L^{-1} min^{-1} with a needled voltage of +4.5 kV. The mobile phase was methanol.

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Table 1
IR bands (cm^{-1}) of the ligand pba and the complexes (1) and (2).

Compound	υ(OH)	υ(=C–H)	υ(C–H)	υ(C=C, or C=N)		$\upsilon(COO^-)$	υ (py or ph)
pba		3060 (w)	2925 (w)	1589 (m) 1472 (m)	1569 (m) 1432 (m)		760 (m) 699 (w)
(1)		3058 (w)	2929 (w)	1604 (m) 1478 (m)	1570 (m) 1440 (m)		770 (m) 704 (m)
(2)	3385 (br)	3058 (w)	2929 (w)	1604 (m)	1478 (m) 1418 (s)	1570 (s, br)	770 (m) 704 (m)

2.2. *Synthesis of the ligand and the Mn(II) complexes*

2.2.1. *Synthesis of the bis(2-pyridylmethyl)benzylamine (pba)*

A mixture of di(2-picolyl)amine (6 mmol, 1.2 g), benzyl bromide (6 mmol, 1.0 g) and Et_3N (6 mmol, 625 mg) in 25 ml of CH_2Cl_2 was stirred at room temperature for 12 h. Then the solution was washed with 20 ml of 1 M NaOH and water, dried with sodium sulfate and concentrated to give oil liquid after column chromatography on silica gel in 80% yield. % Found: C, 78.93; H, 6.65; N, 14.47. % Calc: C, 78.86; H, 6.62; N, 14.52 for $C_{19}H_{19}N_3$. ^1H NMR (400 MHz, $CDCl_3$): $\delta = 3.7$ (s, 2H, CH_2); 3.9 (s, 4H, CH_2N), 7.1–8.5 (m, 13H, H–Ar). ^{13}C NMR (400 MHz, $CDCl_3$): $\delta = 58$ (CH_2); 60 (CH_2N), 118–120 (C–Ar), 118, 136, 148 158, 200 (C-py). IR (KBr) (cm^{-1}): ν(=CH) 3060 m, ν(–CH_2–) 2925 m, ν(C=C, C=N) 1589 s, 1569 m, δ(CH, pyridine) 760 s. UV–vis (H_2O/nm) ($\varepsilon \times 10^{-4}/dm^3\,mol^{-1}\,cm^{-1}$): 203 (4.12), 260 (1.75).

2.2.2. *Synthesis of [$(pba)_2Mn_2Cl_2(\mu\text{-}Cl)_2$] (1)*

To a stirred ethanol solution (5 ml) of bis(2-pyridylmethyl) benzylamine (290 mg, 1 mmol), a solution of $MnCl_2 \cdot 4H_2O$ (213 mg, 1 mmol) in ethanol (5 ml) was added dropwise. The mixture was heated at 80 °C for 2 h and then cooled to room temperature. The solution was filtered and the filtrate was kept in the pyramidal bottle with ether diffusion to precipitate [$(pba)_2Mn_2Cl_2(\mu\text{-}Cl)_2$]. Yield: 75%. % Found: C, 55.04; H, 4.62; N, 10.18; Mn, 13.32. % Calc: C, 54.96; H, 4.61; N, 10.12; Mn, 13.23 for $C_{38}H_{38}Cl_4Mn_2N_6$. UV–vis (H_2O/nm) ($\varepsilon \times 10^{-4}/dm^3\,mol^{-1}\,cm^{-1}$): 218 (1.46), 261 (1.26). Λ_m (DMF/$ohm^{-1}\,cm^2\,mol^{-1}$): 9.6.

2.2.3. *Synthesis of the [$(pba)_2Mn_2(H_2O)_2(\mu\text{-}Ac)_2$] $(Ac)_2$ (2)*

The compound was synthesized by following the same procedure as described in Section 2.2.2 except $MnAc_2 \cdot 4H_2O$ was used. Yield: 70%. % Found: C, 57.58; H, 5.62; N, 8.68; Mn, 11.50. % Calc: C, 57.50; H, 5.66; N, 8.75; Mn, 11.44 for $C_{46}H_{54}Mn_2N_6O_{10}$. UV–vis ($H_2O$/nm) ($\varepsilon \times 10^4/dm^3\,mol^{-1}\,cm^{-1}$): 219 (1.52), 261 (1.00). Λ_m (DMF/$ohm^{-1}\,cm^2\,mol^{-1}$): 256.

2.3. *Reaction of complexes (1) and (2) with hydrogen peroxide*

Reaction process of complexes (1) and (2) with H_2O_2 at 273 K (0 °C) in CH_3CN solution was measured by spectroscopic titration method. The Mn(II)–pba complexes (1) (0.05 mmol) was stirred with an 100 equiv molar amount of hydrogen peroxide in acetonitrile (5 ml) at 0 °C for 2 h, then the reaction mixture was acidified to pH 1 by adding conc. HCl to desalt. The solution was concentrated to 5 ml and the residual material was dissolved into NH_3 aqueous solution, the aqueous solution was extracted with CH_2Cl_2 (3 × 20 ml), dried over Na_2SO_4. After concentrated, oil products were obtained and analyzed by ES-MS and HPLC.

3. Results and discussion

3.1. *Characterization of the Mn(II) complexes*

The elemental analysis, IR and UV data suggest that the ratio of metal/L in the two complexes are 1:1, and the composition of these complexes is [$(pba)_2Mn_2Cl_2(\mu\text{-}Cl)_2$] (1), [$(pba)_2Mn(H_2O)_2(\mu\text{-}Ac)_2$]$(Ac)_2$ (2). The molar conductivity value of the complexes in DMF indicates the complex (1) is a non-electrolyte and the complex (2) is 1:2 electrolyte. The two manganese(II) complexes are soluble in water and common polar organic solvents, insoluble in dichloromethane and ethyl ether.

3.1.1. *IR spectra and mode of bonding*

The IR spectral data of the ligand (pba) and complexes (1) and (2) are listed in Table 1. The IR spectrum of the complex (2) shows a broad band at 3414 cm^{-1} assigned to υ(OH) of the coordinated water, which are confirmed by elemental and thermal analyses. The bands between 2819 and 3060 cm^{-1} for complexes (1) and (2) can be assigned to the stretching vibration of saturated hydrocarbon and arene C–H in the IR spectra. The vibrational spectra of complexes can be used to detect the coordination of the pyridyl nitrogens of the ligands by comparison of the pyridyl ring and in plane vibrations for the free ligands. The pyridyl ring vibration bands at 1589, 1569, 1472 cm^{-1} for complexes (1) and (2) were shifted to 1604, 1570 and 1478 cm^{-1}, respectively. The δ(CH) vibration band (760 cm^{-1}) of pyridyl ring for the complexes was shifted to 770 cm^{-1}. These shifts can be explained by the fact that the nitrogen atoms of pyridyl ring of the ligands donate a pair of electrons each to the central metal forming coordinate covalent bond [12–14]. The strong and wider band at 1570 cm^{-1} and the band at 1418 cm^{-1} for the complex (2) belong to the stretching asymmetric $\nu_{as}(COO^-)$

Table 2
Mass spectra data for the Mn complexes (1) and (2) in methanol solution.

Complexes	*m*/*z* (Relative abundances)	Fragments
[$(pba)_2Mn_2Cl_2(\mu\text{-}Cl)_2$] (1)	380.00 (100)	$[Mn(pba)(Cl)]^+$
[$(pba)_2Mn_2(H_2O)_2(\mu\text{-}Ac)_2$]$(Ac)_2$ (2)	840.75 (70) 822.83 (13) 424.00 (100) 394.00 (47) 290.00 (88)	$[Mn_2(pba)_2(H_2O)(Ac^-)_2 + OH^-]^+$ $[Mn_2(pba)_2(Ac^-)_2 + OH^-]^+$ $[Mn(pba) + OH^- + 2CH_3OH]^+$ $[Mn(pba)(Ac^-)(H_2O) + HAc]^+$ $[(pba) + H^+]^+$
[pba-OH]	306.00 (100) 307.00 (20) (isotopic abundance) 290. 0 (62)	$[(pba\text{-}OH) + H^+]^+$ $[(pba\text{-}OH) + H^+]^+$ $[pba + H^+]^+$

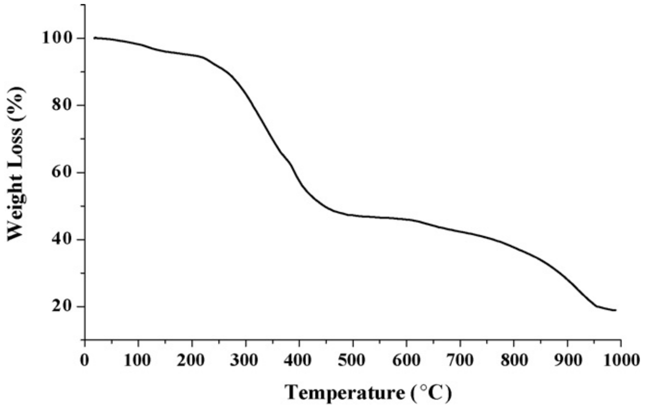

Fig. 1. TG curves in the temperature range 0–1000 °C for the complex (1).

frequencies and the symmetric vibration $\nu_{sym}(COO^-)$, respectively. The $\Delta\upsilon(COO^-)$ between the observed asymmetric $\upsilon_{as}(COO^-)$ and the symmetric $\upsilon_s(COO^-)$ bands could provide important information about the different binding modes of the CH_3COO^- group [15,16]. The difference between $\nu_{as}(COO^-)$ and $\nu_{sym}(COO^-)$ is about 152 cm^{-1}, suggesting that the acetate groups coordinate to the metal atoms only as bidentate ligands [16,17].

3.1.2. Mass spectra

The positive-ion electrospray mass spectra in methanol for the complexes (1) and (2) were shown in Table 2. The main peak at $m/z = 380.00$ (100) for the neutral complex $[(pba)_2Mn_2Cl_2(\mu\text{-}Cl)_2]$ (1) corresponds to the species $[Mn(pdpa)(Cl)]^+$, which was formed by losing the coordinated Cl^- anion. No other species was found indicating the complex (1) is stable in the ES-MS condition. The dominant peak of complex (2) at $m/z = 840.75$ (70) corresponds to the species $[Mn_2(pba)_2(H_2O)(Ac^-)_2 + OH^-]^+$ which indicates the existence of the complex (2). The main peak at $m/z = 424.00$ corresponds to the mononuclear species $[Mn(pba) + OH^- + 2CH_3OH]^+$, which was formed by losing the coordinated H_2O and Ac^- and binding one OH^- and two methanol molecules. The peak at $m/z = 290.00$ (88) corresponds to the species $[(pba) + H^+]^+$ formed by losing the coordinated Mn(II) ion, which indicates the complex (2) is unstable in the ES-MS condition.

3.1.3. Thermal studies

Thermal analysis (TG) curves of the complexes (1) and (2) in the range 0–1000 °C were showed in Figs. 1 and 2. The complex $[(pba)_2Mn_2Cl_2(\mu\text{-}Cl)_2]$ (1) shows four decomposition steps in the temperature range 0–1000 °C (Fig. 1). The 8.55% weight loss in the temperature range 0–250 °C corresponds to the loss of two Cl^- anions (calcd. 8.57%). The loss (29.00%) of two pyridylmethyl group ($2pyCH_2-$) results from the ligands (pba) and one Cl^- ion in the range 250–350 °C (calcd. 28.97%). Other decomposition steps in the range 375–925 °C corresponds to the further decomposition of the two pba ligands in the complex (1). The 15.78% weight loss in the range 350–575 °C indicate the further loss of one benzyl group (calcd. 15.80%).

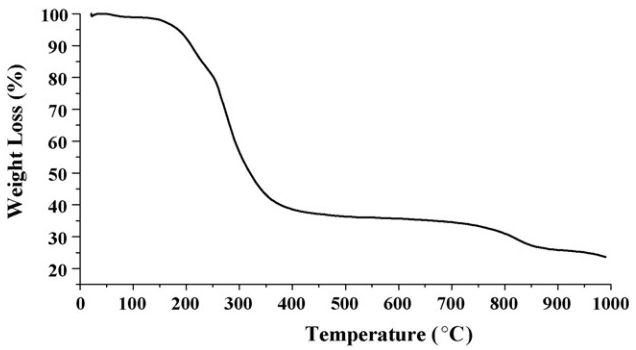

Fig. 2. TG curves in the temperature range 0–1000 °C for the complex (2).

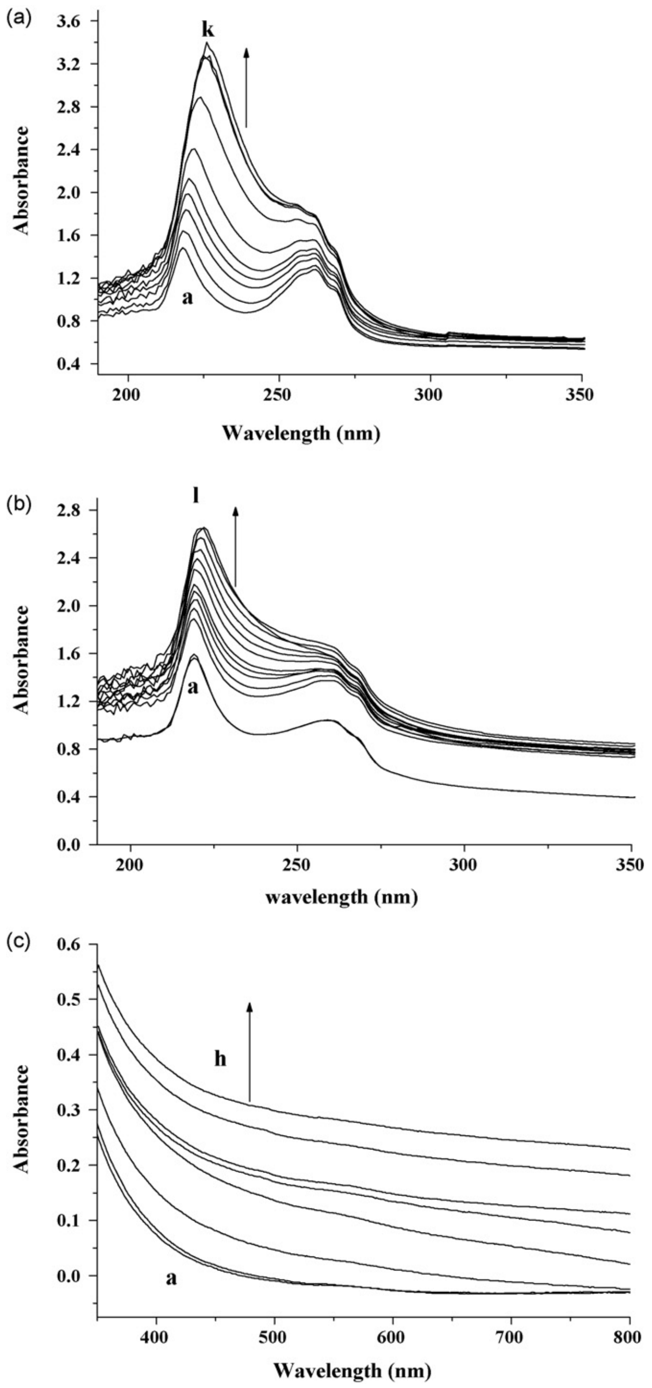

Fig. 3. (a) UV–vis spectral of complex (1) 1×10^{-4} mmol/ml in acetonitrile at 273 K (0 °C) with addition of H_2O_2 over 3 min (line a: $C_{H_2O_2}$, 0 mmol/ml; line k: $C_{H_2O_2}$, 2.94×10^{-4} mmol/ml). (b) UV–vis spectral of complex (2) 1×10^{-4} mmol/ml in acetonitrile at 273 K (0 °C) with addition of H_2O_2 over 3 min (line a: $C_{H_2O_2}$, 0 mmol/ml; line l: $C_{H_2O_2}$, 3.23×10^{-5} mmol/ml). (c) UV–vis spectral of the complex (1) 2.5×10^{-3} mmol/ml in acetonitrile at 0 °C with addition of H_2O_2 over 3 min (line a: $C_{H_2O_2}$, 0 mmol/ml; line h: $C_{H_2O_2}$, 8.82×10^{-5} mmol/ml).

The forth step of decomposition occurs at a temperature range from 580 to 940 °C corresponds to the loss of one benzyl amine ($phCH_2NH_2$) with a weight loss 21.98% (calcd. 22.03%). So the data of thermal analysis shows the existence of the dinuclear manganese(II) complex (1).

The thermal decomposition of the $[(pba)_2Mn_2(H_2O)_2(\mu\text{-}Ac)_2](Ac)_2$ (2) proceeds approximately with three decomposition steps. There is no obvious weight loss in the 0–115 °C. The first step falls in the range of 115–225 °C, which is assigned to loss of two coordinated H_2O molecules and two CH_3COO^- anions with a weight loss 16.11% (calcd. 16.03%). The weight loss 44.72% in the range of 225–475 °C is assigned to loss of four pyridylmethyl group ($4pyCH_2-$) and one CH_3COO^- anions (calcd. 44.65%). The final decomposition step in the range of 475–900 °C corresponds to the loss of one benzyl amine ($phCH_2NH_2$) with a weight loss 10.99% (calcd. 11.13%). The thermal decomposition data obtained supports the proposed structure of the complex (2).

3.2. Reaction of complexes (1) and (2) with H_2O_2 by spectroscopic titration

Reaction of complexes (1) and (2) with H_2O_2 at 273 K (0 °C) in CH_3CN solution by spectroscopic titration was showed in Fig. 3(a)–(c). In the UV–vis spectrum, the two absorption bands at around 218 and 261 nm were assigned to π–π^* and n–π^* intraligand transition [18]. The addition of H_2O_2 to the complexes (1) and (2) solution promoted an absorbance increase in the 200–800 nm (Fig. 3(a)–(c)), typical of metal center oxidation [19]. The bands at 261 nm slowly increase with broadening while the bands at 218 nm experience a slight increase in intensity with slight red shift. These changes suggest the presence of a slight amount of a protonated form, or the formation of a mixture of oxo bridged species on the interaction of Mn complexes with H_2O_2 [20,21].

The intramolecular hydrogen atom abstraction and H_2O_2 rebound or direct H_2O_2 insertion mechanism through the intermediate for the benzylic hydroxylation reaction was proposed by Itoh and co-workers, although such an intermediate could not be detected at room temperature [21–25]. Intramolecular aromatic ligand hydroxylation was unambiguously confirmed by the modified ligands pba-OH (m/z = 306) isolated by demetalation of the final products (Table 2). The yield of hydroxylated ligand pba-OH was evaluated as about 65% based on the manganese complex (1) by comparing the dimension of the peak at 17 min (bpa) with that at 19 min (pba-OH) in HPLC.

4. Conclusion

The dinuclear Mn(II) complexes of bis(2-pyridylmethyl) benzylamine (bpa) could react with H_2O_2 resulting active oxidants, which lead to the intramolecular aromatic hydroxylation. This experimental result is helpful to understand the mechanisms of oxygen transfer reactions catalyzed by non-heme dioxygenases.

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