Structure and Photosynthetic Mimicking of Bis(2,6-bis(benzimidazol-2-yl)pyridine)manganese(II)

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$Mn(bzimpy)_2$(1) [bzimpy = 2,6-bis(benzimidazol-2-yl)pyridine], a mononuclear manganese(II) complex, was synthesized by the reaction of $Mn(OOCMe)_2$ with bzimpy in absolute ethanol. The complex was structurally characterized by elemental analysis, cyclic voltammetry, and X-ray crystallography. In the complex, the manganese-nitrogen distances were different, and the geometry and the metal ion environment showed the distortion. The cyclic voltammetric measurements have been performed to assess its redox characteristics. The presence of oxidation wave at +0.62 V and +0.81 V vs. SCE or +0.8 V and +1.0 V vs. NHE suggested that this complex could catalyze the oxidation of water, therefore, simulate the water-oxidizing complex (WOC) of photosystem II (PS II). The measurements of photoreduction of 2,6-dichlorophenolindophenol (DCPIP), and oxygen evolution in the manganese-depleted and the complex 1-reconstituted PS II preparations just support our conjecture.

Keywords 2,6-bis(benzimidazol-2-yl)pyridine (bzimpy), crystal structure, photosynthetic mimiking

Introduction

Manganese ions play an important role in the light-induced oxidation of water to molecular oxygen in photosystem II (PS II) of green plants.[1-3] In recent years, manganese complexes of polypyridine ligands, such as bipyridine, 1,10-phenanthroline and 2,2′:6′,2″-terpyridine, have had considerable attention as the complexes formed are useful models for manganese-containing bimoleculars.[4-6] Therefore, synthesis and characterization of manganese in its various oxidation states, with various ligand types and nuclearities, have contributed substantially to our understanding of the role and mechanism of manganese complexes in photosynthesis.

The prevalent notion is that the water-oxidizing complex (WOC) of PS II is a tetranuclear manganese cluster. The current model for the assembly of the manganese cluster of WOC during photoactivation indicates that the first two manganeses are integrated sequentially followed by the relatively slow attachment of the two additional manganese atoms.[7-9] From this point of view, the mononuclear manganese complex may also be able to bring about the sequential addition of four individual manganese atoms and reconstitute WOC.

Ligand of the title complex comprises a donor group of relevance to the coordination of metal centers in many biological systems, namely imidazole (hisdidine). Thus, here we report the synthesis, crystal structure and electrochemical characterization of complex **1**, $Mn(bzimpy)_2$[bzimpy = 2,6-bis(benzimidazol-2-yl)pyridine], and its photosynthetic mimicking.

Experimental

Materials and methods

Ethanol and dimethylsulfoxide were purified by distillation. Tetrabutylammonium hexafluorophosphate was obtained from Wako Chemical Co. and manganese acetate was from Aldrich. The bzimpy was prepared from 2,6-pyridinedicarboxylic acids as the reported method.[10] PS II membrane was prepared from spinach as described by Kuwabara and Murata.[11] Extraction of Mn was performed as the method reported previously.[12]

Preparation of the title complex **1**

The complex was prepared by addition of $Mn(OAc)_2$ (0.09 g, 0.26 mmol) in ethanol (10 mL) to a stirred solution of 2,6-bis(benzimidazol-2-yl)pyridine (0.16 g, 0.538 mmol) in absolute ethanol (30 mL). The resulting solution was stirred at 50 ℃ for 30 min and yellow precipi-

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tate was collected by filtration, washed with ethanol, and dried *in vacuo*. The precipitate was dissolved in dimethylsulfoxide and the solution was filtered. The filtrate was layered with EtOH to produce yellow crystal in one week (yield 0.09 g, 52%). M. p. 428—431 ℃; FT-IR (KBr) ν: 3054, 1601, 1574, 1502, 1450 cm^{-1}. Anal. calcd for $C_{38}H_{24}MnN_{10}$: C 67.4, H 3.6, N 20.7; found C 67.5, H 3.8, N 20.5.

X-Ray crystallographic data collection and refinement of structure

Single crystal of the complex **1** was selected and mounted on the goniometer of Rigaku R-AXIS RAPID imaging plate diffractometer. Diffraction data were collected at 293 K with graphite monochromated Mo Kα radiation ($\lambda = 0.07107$ nm) operating at 50 kV and 3 mA. The detector swing angle was 5.00°. Readout was performed in the 0.100 mm pixel mode. Absorption corrections were applied by correlation of symmetry-equivalent reflections using the ABSOR program. Data reduction was performed by SHELX97 (Sheldrick, 1997). The structure was solved by direct method and difference Fourier map using SHELXS97 (Sheldrick, 1997) and refined on F^2 by full-matrix least-squares techniques using SHELXL97 (Sheldrick, 1997). The data collection and structure solution parameters and conditions are listed in Table 1. Selected bond lengths and angles are listed in Tables 2 and 3.

Table 1 Crystallographic data of complex $Mn(bzimpy)_2$

Empirical formula	$C_{38}H_{24}N_{10}Mn$
Formula weight	675.61
Crystal size (mm)	0.35×0.14×0.11
Crystal color	Yellow
Crystal system	Monoclinic
Space group	*Pn*
a (nm)	1.02422(18)
b (nm)	1.01588(12)
c (nm)	1.6012(2)
β (°)	90.72(3)
V (nm^3)	1.6659(4)
Z	2
T (K)	293(2)
$D_{calc.}$ (Mg/m^3)	1.347
Absorption coefficient (mm^{-1})	0.440
F(000)	694
θ Range for data collection	2.00—27.48
Reflections collected/unique	6041/6037 [$R_{int} = 0.1330$]
Completeness to $\theta = 27.48$	94.9%
Data/restraints/parameters	6037/2/447
Goodness of fit on F^2	0.948
Final *R* indices [$I > 2\sigma(I)$]	$R = 0.0717$; $wR = 0.1830$
Largest difference peak and hole (e/nm^3)	267 and −288

Table 2 Selected bond lengths (nm) for $Mn(bzimpy)_2$

Atom	Bond length	Atom	Bond length
Mn(1)—N(3)	0.2220(6)	Mn(1)—N(5)	0.2229(7)
Mn(1)—N(10)	0.2230(6)	Mn(1)—N(8)	0.2253(6)
Mn(1)—N(1)	0.2239(6)	Mn(1)—N(6)	0.2265(6)
N(1)—C(6)	0.1354(9)	N(1)—C(7)	0.1364(9)
N(2)—C(7)	0.1348(9)	N(2)—C(1)	0.1396(10)
N(3)—C(12)	0.1325(10)	N(3)—C(8)	0.1365(10)
N(6)—C(26)	0.1353(9)	N(6)—C(25)	0.1390(10)
N(7)—C(26)	0.1356(10)	N(7)—C(20)	0.1391(10)
N(8)—C(27)	0.1327(10)	N(8)—C(31)	0.1354(10)
C(1)— C(2)	0.1368(11)	C(4)—C(5)	0.1360(13)
C(1)—C(6)	0.1401(10)	C(2)—C(3)	0.1340(12)
C(3)—C(4)	0.1428(13)	C(5)—C(6)	0.1438(10)
C(7)—C(8)	0.1445(10)	C(8)—C(9)	0.1440(11)
C(9)—C(10)	0.1320(15)	C(10)—C(11)	0.1377(14)
C(11)—C(12)	0.1396(11)	C(30)—C(31)	0.1391(11)
C(20)—C(21)	0.1369(12)	C(20)—C(25)	0.1426(11)
C(21)—C(22)	0.1405(13)	C(22)—C(23)	0.1403(13)
C(23)—C(24)	0.1394(13)	C(24)—C(25)	0.1360(11)
C(26)—C(27)	0.1491(11)	C(27)—C(28)	0.1357(11)
C(28)—C(29)	0.1349(16)	C(29)—C(30)	0.1397(15)

Table 3 Selected bond angles (°) for $Mn(bzimpy)_2$

Atom	Angle	Atom	Angle
N(1)-Mn(1)-N(5)	145.2(2)	N(5)-Mn(1)-N(10)	105.0(2)
N(1)-Mn(1)-N(3)	73.0(2)	N(1)-Mn(1)-N(10)	84.8(2)
N(3)-Mn(1)-N(5)	72.2(2)	N(5)-Mn(1)-N(8)	107.8(2)
N(3)-Mn(1)-N(8)	179.1(3)	N(1)-Mn(1)-N(8)	107.0(2)
N(6)-Mn(1)-N(10)	145.0(2)	N(3)-Mn(1)-N(6)	107.8(2)
N(6)-Mn(1)-N(8)	71.3(2)	N(8)-Mn(1)-N(10)	73.7(2)
N(5)-Mn(1)-N(6)	85.9(2)	N(6)-Mn(1)-N(1)	105.2(2)
N(3)-Mn(1)-N(10)	107.2(2)		

Measurements

The FT-IR spectra were measured as KBr pellets on a Perkin-Elmer System 2000 spectrometer. Elemental analyses were carried out on a Carlo-Erbla 1160 elemental analyzer. Electrochemical measurements were recorded using a CHI 705A Electrochemical Analyzer. The cyclic voltammetry was conducted in a standard three-electrode cell. A glassy carbon electrode (2 mm diameter) was used as the working electrode; a platinum wire as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode. The scan rate was 30 $mV \cdot s^{-1}$. Anhydrous dimethyl sulfoxide was used as the solvent. The supporting electrolyte was tetrabutylammonium hexafluorophosphate (0.1 mol/L). The rate of oxygen evolution was monitored at 20 ℃ with a Clark-type electrode.[13] The assay medium contained the preparations of PS II membrane at a concentration of 10 μg Chl/mL, 25 mmol/L Mes-NaOH (pH = 6.5), 5 mmol/L $CaCl_2$, 10 mmol/L NaCl, 300 mmol/L sucrose and 200 μmol/L phenyl-*p*-benzoquinone, 300 μmol/L potassium ferricyanide as electron acceptor. The photoreduction of 2,6-dichlorophenolindophenol (DCPIP) was measured at 20 ℃ using a spectrophotometer (Shimadzu UV-160 lpc UV-visible). The reaction medium consisted of the preparations of PS II membrane at a concentration of 10 μg Chl/mL, 20 mmol/L Tris-HCl (pH 7.8), 10 mmol/L NaCl, 2 mmol/L $MgCl_2$ and 50 μmol/L DCPIP.

Results and discussion

Crystal structure

The structure of complex **1** and the atom numbering scheme are shown in Fig. 1. Selected bond lengths and bond angles are listed in Tables 2 and 3, respectively.

The complex shows that the expected structure with two meridionally coordinated tridentate bzimpy ligands gives a distorted octahedral coordination of the manganese as observed for $[Mn(terpy)_2]^{2+}$ in $Mn(terpy)_2(I_3)_2$.[14] Two Mn—N_{py} bonds in complex **1** are almost co-linear [N_3-Mn_1-N_8, 179.1(3)°] as found in $[Mn(terpy)_2]^{2+}$ where the equivalent angle is 177.1(5)°, and in $[Fe(bzimpy)_2]^{2+}$ where the equivalent angle is 176.8(4)°.[15] The average N-Mn-N chelate angle is 72.5° compared with 79.5° for $[Fe(bzimpy)_2]^{2+}$ and 80.6° for $[Mn(terpy)_2]^{2+}$ complex.

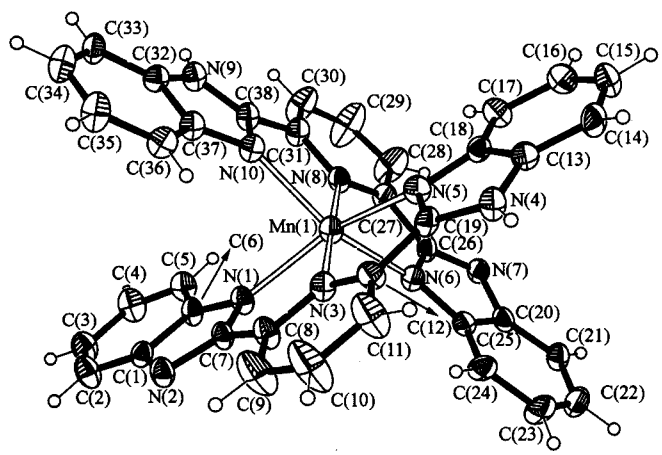

Fig. 1 Structure of the complex $Mn(bzimpy)_2$.

The average Mn—N bond distance (0.2239 nm) in $Mn(bzimpy)_2$ is identical to the value for $[Mn(terpy)_2](I_3)_2$ (0.2232 nm) within experimental error. The Mn—N bond length in $[Mn(terpy)_2]^{2+}$ shows considerable asymmetry, *i.e.*, the Mn—$N_{central}$ distances are nearly 0.006(2) nm shorter than the Mn—$N_{terminal}$ distances. Similarly, the Fe—N_{py} bond distances are also shorter than the other Fe—N distances in $[Fe(bzimpy)_2]^{2+}$ by 0.006(1) nm. In $Mn(bzimpy)_2$, there is a distortion of the coordination sphere in which the average Mn—N_{py} distance, 0.2237(1) nm, is slight shorter than the average of other Mn—N distance, 0.2241(4) nm. The distortion can always be observed in terpyridyl complexes of the first-row transition metal complexes,[16-18] which was thought to be due to better overlap of the metal t_{2g} orbitals with the π^* orbitals of the central pyridyl group in comparison with the distal pyridyl groups.[19] In addition, the MnN_6 coordination shows appreciable angular distortions. The N_1-Mn_1-N_3, N_5-Mn_1-N_3, N_6-Mn_1-N_8, and N_{10}-Mn_1-N_8 angles deviate from 90° by 17°, 17.8°, 18.7° and 16.3°, respectively.

The crystal packing shows that the $Mn(bzimpy)_2$ molecules are packed in planes. The complex **1** features a

layer crystal structure, which may be conveniently described with reference to the hydrogen bonds scheme shown in Fig. 2. Each ligand formed two hydrogen bonds: (A) N—H···N (B), 0.2778 nm, and (A) N···H—N (C), 0.2741 nm, where A, B, C represent different molecules, and N is uncoordinated nitrogens of the benzimidazole rings. The lattice of parameters complex **1** can be contrasted with that of a similar complex, [Mn(bzimpy)$_2$]·EtOOCMe·H$_2$O, in which the crystal space group is *Cc* [a = 1.3644(1) nm, b = 1.5309(2) nm, c = 1.8558(3) nm, β = 110.28(1)°].[20] Although both of them are built from the same ligand, their packing modes are different, which may contribute to the subsistence of the solvent molecules inside the crystal of [Mn(bzimpy)$_2$]·EtOOCMe·H$_2$O.

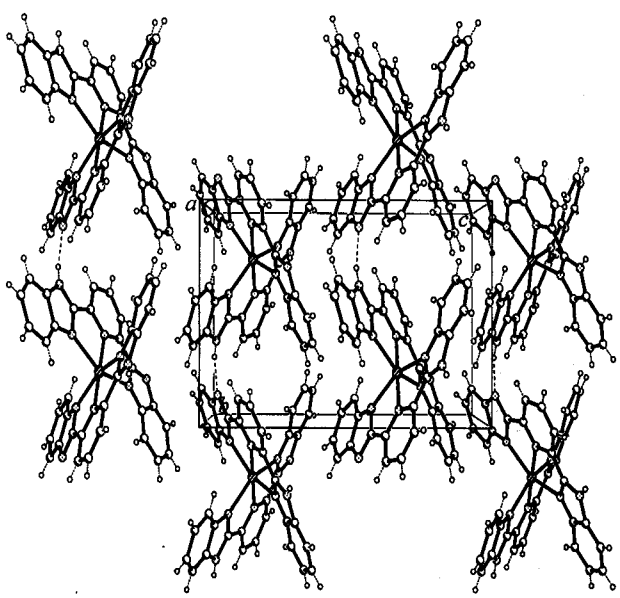

Fig. 2 Representation of the crystal packing in Mn(bzimpy)$_2$. The dotted lines represent the H-bonding interactions N—H···N.

Photosynthetic mimicking

Cyclic voltammetry

A necessary criterion for the design of model systems for the water oxidation reaction in PS II is that the model system must have redox potential more (or at less as) positive than (as) the minimum of +0.6 V vs. NHE required to oxidize water to oxygen at pH 7 in the biomembrane.[21] So the redox potential of complex **1** was examined by cyclic voltammetery. The result shows two oxidation peaks in the positive potential region (Fig. 3). The literature data abound with a diversity of redox potentials for Mn(II)—Mn(III) and Mn(III)—Mn(IV) couples.[22-25] In light of literature values, the waves of +0.62 V and +0.81 V vs. SCE for the complex **1** can be assigned to two successive oxidations of Mn(II) to Mn(III) and Mn(IV).

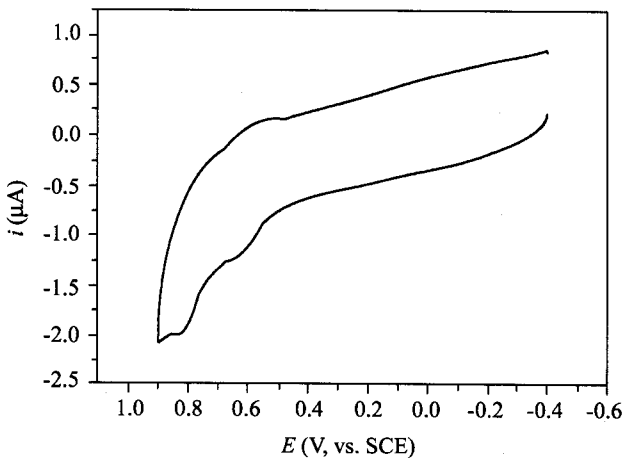

Fig. 3 Oxidative voltammogram of the complex Mn(bzimpy)$_2$ in dimethyl sulfoxide.

Additionally, the complex **1** undergoes two reduction processes in negative potential region of −1.2 V to −1.8 V vs. SCE (Fig. 4), which may be assigned to the reduction process of the ligand itself. Assignment of the ligand-centered reduction peaks was based on a recent study of manganese, cobalt and iron complexes with a variety of ligands.[26]

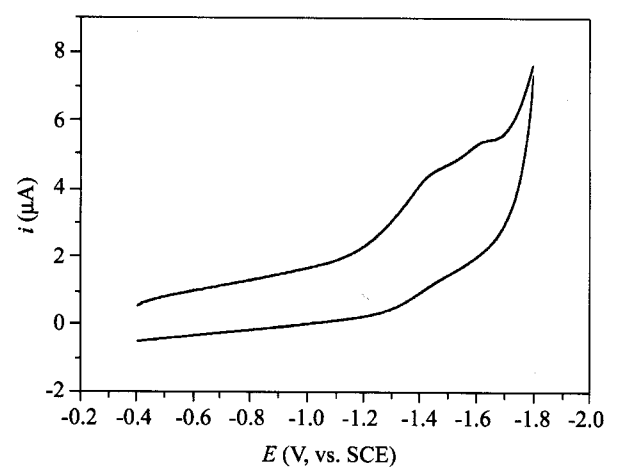

Fig. 4 Reductive voltammogram of the complex Mn(bzimpy)$_2$ in dimethyl sulfoxide.

Because the complex **1** with its oxidation potential at +0.62 and 0.81 V vs. SCE or *ca.* +0.8 and 1.0 V vs. NHE is obviously more positive than +0.6 V vs. NHE that required for the water oxidation at pH 7 in the photosystem,[21] we further performed the measurements of photoreduction of DCPIP and oxygen evolution in the manganese-depleted PS II and the complex **1** reconstituted PS II preparations.

Photoreduction of DCPIP *and oxygen evolution measurements*

Reconstruction of electron transport capacity was

demonstrated by the experiments using DCPIP as the final electron acceptor (Fig. 5). The initial rate of DCPIP photoreduction in Mn-depleted preparations was severely reduced in comparison with native PS II preparations (control). Photoreduction was greatly restored in the presence of either $MnCl_2$ or the complex **1**. The oxygen-evolving activities of the PS II membrane and the other reconstructed Mn-depleted preparations are listed in Table 4. The oxygen activity was almost completely inhibited in the Mn-depleted samples, and can be partially recovered when $MnCl_2$ was added. Moreover, the addition of complex **1** yielded an even greater initial rate of oxygen evolution than that in the reconstructed $MnCl_2$, as shown in Table 4.

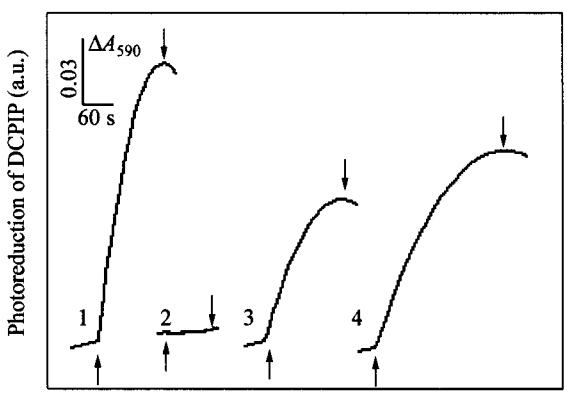

Fig. 5 Photoreduction of DCPIP measured at 590 nm in DT20 preparations. Trace 1, control; trace 2, Mn depleted; trace 3, reconstituted with 1 μmol/L $MnCl_2$; trace 4, reconstituted with 1 μmol/L complex **1**.

Table 4 Reactivation of oxygen evolution in Mn-depleted preparations[a]

	Initial rate of oxygen evolution (μmol O_2/mg Chl h)
Native preparations	268
Mn-depleted	0
Mn-depleted + $MnCl_2$	37
Mn-depleted + Mn complex	88

[a] $MnCl_2$ and Mn complex were added at a concentration of 2 μmol/L.

Observations of electron transport and oxygen evolution obviously show that Mn complex can reconstruct the WOC in Mn-depleted PS II preparations. It is noteworthy that complex **1**, as an electron donor, is more efficient than Mn-Niten complex and Mn-Salhxn complex.[27] It is likely that the complex **1** contains pyridine and benzimidazole rings, which facilitate interaction with the exposed donor side of PSII. Therefore, the complex **1** gains more accessibility to the Mn oxidation sites in the protein matrix, which brings about the restore of DCPIP photoreduction and higher rates of oxygen evolution after the reconstruction.

Above all, our results clearly demonstrate that mononuclear complex **1** is able to reconstitute the WOC of PS II in plant photosynthesis with a significantly greater efficiency.

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