

Synthesis and Characterization of Two Novel High Valent Dinuclear Complexes with a Triphenolate Ligand Bearing Functional Groups

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Abstract: Two novel high valent complexes $[M_2(\text{III}, \text{III})L(\mu\text{-OAc})_2]\cdot\text{PF}_6$ ($M=\text{Mn}, \text{Fe}$; **9**) were prepared, where L was the *tri*-anion of 2,6-bis{[(2-hydroxy-3-(morpholin-4-yl methyl)-5-*tert*-butyl benzyl)(pyridyl-2-methylamino)methyl]-4-methyl phenol} which contained additional phenolic, *tert*-butyl and morpholin-4-yl methyl groups compared to its parent $[\text{Mn}_2(\text{II}, \text{II})(\text{bpmp})(\mu\text{-OAc})_2]\cdot\text{ClO}_4$ (**10**). These improvements decreased the difference between the new model and $(\text{Mn})_4$ cluster (OEC in nature).

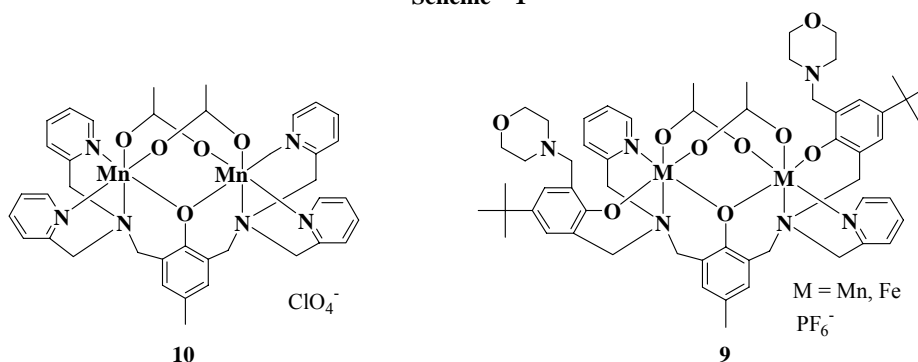
Keywords: Dinuclear complex, OEC, artificial photosynthesis.

Artificial photosynthesis provides a valuable attempt for finding continuable energy resources¹. Much research effort has been aimed at oxygen evolving center (OEC) in donor side of natural photosystem II, which is responsible for the oxygenic atmosphere on the earth and provides the electrons needed for producing energy rich product by CO_2 reduction². $[\text{Mn}_2(\text{II}, \text{II})(\text{bpmp})(\mu\text{-OAc})_2]\cdot\text{ClO}_4$ (**10** in **Scheme 1**) [Hbpmp: 2,6-bis{[N, N-di(pyridyl-2-methylamino)methyl]-4-methyl phenol}] is a meaningful model for donor side of PS II in recent research, in which the *p*-cresol and DPA arms functionally mimic the Tyr_z and His190 in natural photosystem, respectively³. This model needs further improvement. The complex of $[\text{M}_2(\text{III}, \text{III})L(\mu\text{-OAc})_2]^+$ ($M = \text{Mn}, \text{Fe}$; **9** in **Scheme 1**) is a new model in which two phenolic groups replaced two pyridyl groups, resulting higher valence of central Mn ions from coordination with phenol anionic oxygen instead of pyridyl neutral nitrogen. In the result, the oxidative activity of the new model can be increased compared to **10**. Although the exact mechanism of water oxidation is not very clear, it is known that higher oxidation state of Mn(III) plays an important role in this process, and the increase of the amount of anionic functional groups of ligand can stabilize higher oxidation state of manganese⁴. Fe was introduced to study the influence of central ions other than Mn on oxidative activity of the complex. As donors, the *tert*-butyl and morpholin-4-yl methyl on the phenol can further improve coordination ability

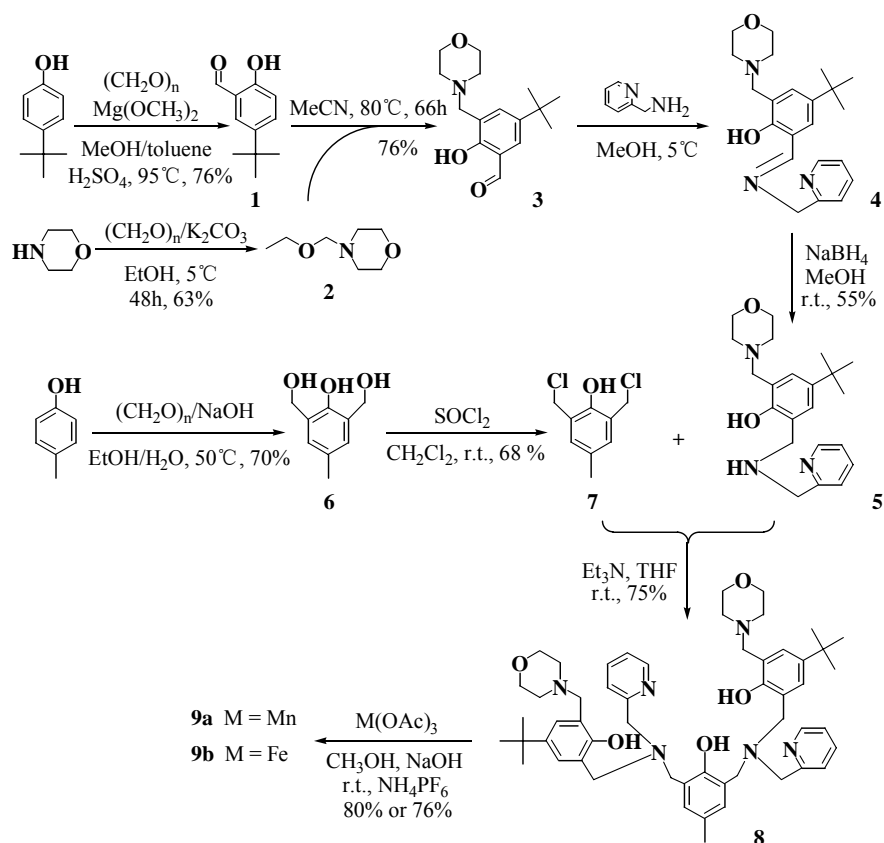
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of oxygen by increasing its electronic density *via* resonance effect. Synthesis and characterization of $[M_2(\text{III}, \text{III})L(\mu\text{-OAc})_2]\cdot\text{PF}_6$ is discussed in this paper.

Scheme 1



Scheme 2



Experimental

All materials were reagent grade or better. The chemicals were used as purchased, but the solvents were dried by standard methods just before used.

The ESI-MS experiments were performed on a HP1100LC/MSD mass spectrometer. The ^1H and ^{13}C NMR measurements were performed on a Varian INVOA 400 MHz spectrometer. The IR absorption spectra were recorded with a JASCO FT/IR 430 spectrometer. UV/Vis spectra were recorded on a HP 8453 spectrometer in acetonitrile. Cyclic voltammetry and differential pulse voltammetry were measured on a BAS100W potentiostat in acetonitrile. All potentials reported were vs. SCE.

5 and **7** were prepared *via* modified literature methods^{5,6}.

Synthesis of ligand **8**. The solution of **7** (0.33 g, 1.6 mmol), **5** (1.20 g, 3.3 mmol) and several drops of Et_3N in THF was stirred at ambient temperature for 1 hour. The solvent was evaporated. Purification on silica gel using $\text{EtOAc}/\text{CH}_3\text{OH}$ (95:5) as eluent gave 1.1 g (75%) of desired product.

Synthesis of complex **9**. NaOH (1 mol/L, 0.1 mL) and $\text{M}(\text{OAc})_3(\text{H}_2\text{O})_n$ ($\text{M} = \text{Mn}$, Fe ; 0.45 mmol) were added to the solution of **8** (150 mg, 0.22 mmol) in CH_3OH (2 mL) at stirring. The mixture was stirred for 30 min at ambient temperature then filtered. 1 mL of saturated NH_4PF_6 (aq.) was added to the solution. The resulting mixture was kept at 0°C for 12 hours for complete precipitation. The solid was filtrated and washed with cool methanol. After drying, the products were obtained.

The structures of new compounds were confirmed by the analysis of NMR, MS, IR, UV/Vis and electrochemistry⁷.

Results and Discussion

Results from differential pulse and cyclic voltammograms show that the introduction of phenolic groups made the formation of $\text{Mn}_{\text{III,IV}}/\text{Mn}_{\text{III,III}}$ possible. And the Fe ions made the potentials of $\text{Fe}_{\text{III,IV}}/\text{Fe}_{\text{III,III}}$ more positive than $\text{Mn}_{\text{III,IV}}/\text{Mn}_{\text{III,III}}$, which can increase the oxidative activity of the complex.

Table 1 Electrochemical data in acetonitrile

Complex	$E_{1/2}/V^a(\Delta E_p/\text{mv})$			
	$\text{M}_{\text{II, III}}/\text{M}_{\text{II, II}}$	$\text{M}_{\text{III, III}}/\text{M}_{\text{II, III}}$	$\text{M}_{\text{III, IV}}/\text{M}_{\text{III, III}}$	b
9a	-0.15 (168)	0.19 (166)	0.73 (167)	1.50 (40)
9b	-0.64 (187)	-0.18 (149)	1.22 (192)	1.81 (142)
10	0.50 (70)	1.06 (120)	— ^c	—

a. From cyclic voltammetry in CH_3CN with 0.1 mol/L TBAPF_6 as supporting electrolyte, $\nu = 100 \text{ mV}\cdot\text{s}^{-1}$. b. The final oxidation product is a monomeric M_{II} or possibly M_{IV} . c. No oxidation to the $\text{Mn}_{\text{III, IV}}$ state in CH_3CN .

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7. **8**: IR (KBr, ν , cm^{-1}): 2958, 2907, 2860, 1619, 1572, 1482, 1386, 1363, 1303, 1116, 810, 756; ^1H NMR (CDCl_3 , 400 MHz, δ ppm): 1.24 (s, 18H, Ph-*tert*-butyl), 2.21 (s, 3H, Ph- CH_3), 2.54 (s, 8H, $\text{NCH}_2\text{CH}_2\text{O}$), 3.64 (s, 4H, morpholine- CH_2 -Ph), 3.72 (s, 8H, $\text{NCH}_2\text{CH}_2\text{O}$), 3.72 (s, 4H, *p*-cresol- CH_2N), 3.75 (s, 4H, *tert*-butyl-Ph- $\text{CH}_2\text{N}(\text{CH}_2)_2$), 3.83 (s, 4H, Py- CH_2N), 6.92 (s, 2H, *p*-cresol), 6.97 (d, 2H, $J = 2.0$ Hz, *tert*-butyl-Ph), 7.13 (d, 2H, $J = 7.9$ Hz, Py), 7.13 (d, 2H, $J = 2.5$ Hz, *tert*-butyl-Ph), 7.44 (d, 2H, $J = 7.9$ Hz, Py), 7.61 (td, 2H, $J = 7.7, 1.5$ Hz, Py), 8.53 (d, 2H, $J = 4.4$ Hz, Py); ^{13}C NMR (CDCl_3 , 100 MHz, δ ppm): 20.72, 31.73, 34.04, 53.11, 54.56, 54.68, 59.80, 60.20, 66.94, 120.69, 122.11, 122.94, 123.27, 123.40, 125.71, 126.84, 127.55, 129.89, 136.54, 141.36, 148.92, 153.84, 154.01, 158.82; ESI-MS (m/z): 871.5 (calcd. for $[\text{M}+\text{H}]^+$, 871.55), 893.5 (calcd. for $[\text{M}+\text{Na}]^+$, 893.55); **9a**: IR (KBr, ν , cm^{-1}): 2954, 2907, 2868, 1608, 1489, 1569, 1430, 1384, 1362, 845, 798, 760, 557; UV-vis (λ_{max} , nm): 258, 365; ESI-MS (m/z): 1096.3 (calcd. for $[\text{M}-\text{PF}_6]^-$, 1095.42); **9b**: IR (KBr, ν , cm^{-1}): 2956, 2910, 2865, 1608, 1481, 1575, 1439, 1400, 1361, 845, 799, 758, 557; UV-vis (λ_{max} , nm): 286, 345; ESI-MS (m/z): 1097.3 (calcd. for $[\text{M}-\text{PF}_6]^-$, 1097.41).

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