JOURNAL OF CHEMICAL RESEARCH 2004 JANUARY, 57–58 **RESEARCH PAPER** 57

Synthesis and characterisation of a high valent dinuclear Mn(III,III) complex of a triphenolate ligand $[N_4O_3]^{3-}$ with two extra functional groups

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A new high valent complex $[Mn_2(III,III)L(\mu\text{-}OAc)_2]\cdot PF_6$ **7** was prepared, where L was the *tri*-anion of 2,6-Bis{[(2-hydroxy-5-*tert*-butylbenzyl)(pyridyl-2-methyl)amino]methyl}-4-methylphenol which contained two additional phenolate groups and two *tert*-butyl groups compared to its parent $[Mn_2(II,II)(bpmp)(\mu\text{-}OAc)_2]\cdot PF_6$. These improvements narrowed the disparity between the new model and $(Mn)_4$ cluster (OEC in nature).

Keywords: dinuclear manganese, ligand design, artificial photosynthesis

Artificial photosynthesis is a target in the such for continuable energy resources.[1] Much research effort has been aimed at the oxygen evolving centre (OEC) on the donor side of natural photosystem II, which is responsible for the oxygenic atmosphere on earth and provides the electrons needed for producing energy-rich reduced carbon product by reducing CO_2.[2] $[Mn_2(II,II)(bpmp)(\mu\text{-}OAc)_2]\cdot PF_6$ [Hbpmp: 2,6-Bis {[N,N-di(pyridyl-2-methyl)amino]methyl}-4- methylphenol] 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 respectively.[3] But many improvements are needed for this model. The following complex of $[Mn_2(III,III)L(\mu\text{-}OAc)_2]^+$, where L is the *tri*-anion of 2,6-Bis{[(2-hydroxy-5-*tert*-butylbenzyl)(pyridyl-2-methyl) amino]methyl}-4-methylphenol, is a new model which decreases the difference from the $(Mn)_4$ cluster (OEC in nature). In this complex, two pseudo-octahedrally coordinated Mn ions are bridged by a phenolate group and two bidentate acetate ligands. Compared to Hbpmp, its two phenolic groups replace two pyridyl groups, and the resulting higher valence of the central Mn ions from coordination with phenol anionic oxygen instead of pyridyl neutral nitrogen can increase the oxidative activity of the OEC in light-driven water oxidation. Although the exact mechanism of water oxidation is not very clear, it is known that the Mn(III) oxidation state and higher plays an important role in this process, and the increase of the amount of anionic functional groups of ligands can stabilise higher oxidation states of manganese.[4] In $[Mn_2(III,III)L(\mu\text{-}OAc)_2]\cdot PF_6$, the stronger coordinate bond between anionic oxygen of phenolate groups and Mn than between neutral nitrogen of pyridine and Mn can enhance chelation of a ligand, then prevent the dissociation of central ions as in $[Mn_2(II,II)(bpmp)(\mu\text{-}OAc)_2]\cdot PF_6$. The *tert*-butyl on the phenoxide can further improve the coordination ability of the oxygen atom by increasing its electronic cloud density via resonance effects. Simultaneously *para* orientation of *tert*-butyl than *ortho* orientation to the hydroxyl decreases the steric hindrance when a water molecule attacks the reaction centre. The solubility of the ligand is also improved remarkably by the introduction of *tert*-butyl groups, and the whole ligand maintains the structural ascendency of Hbpmp in analogy with Tyr_z and His190. The synthesis and characterisation of $[Mn_2(III,III)L(\mu\text{-}OAc)_2]\cdot PF_6$ is presented in this paper.

Experimental

All materials were reagent grade or better. The chemicals were used as purchased, but the solvents were dried by standard methods just before use. 2,6-Bis(hydroxymethyl)-4-methylphenol and 2,6-bis(chloromethyl) -4-methylphenol were prepared by literature methods.[5]

The electrospray ionisation mass spectrometry (ESI-MS) experiments were performed on a HP1100LC/MSD mass spectrometer. Electrospray conditions were capillary voltage: 4kV; bath and nebulising gas: nitrogen; nebulising temperature: 350°C; pressure: 310.26 kPa. The drying nitrogen gas flow was 5.0 l per min. The liquid flow was 0.2 ml per min. The solvent was acetonitrile or methanol/water. Microanalyses data were obtained on a MOD 1046 instrument. The ^1H NMR and ^{13}C NMR measurements were performed on a Varian INVOA 400 MHz spectrometer for 1D or 2D in chloroform-*d*. 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 containing tetrabutylammonium hexafluorophosphate as supporting electrolyte. The three-electrode system comprised a glassy carbon disc (diameter 3 mm) as working electrode, a nonaqueous Ag/Ag^+ electrode (10 mM $AgNO_3$ in acetonitrile) as reference electrode and Pt as counter electrode. The reference electrode has a potential of –0.08 V *vs* the ferrocene/ferrocenium couple in acetonitrile as an external standard. All potentials reported were *vs* SCE.

2-Hydroxy-5-tert-butylbenzaldehyde (**1**): This compound was prepared according to a procedure described by Aldred *et al.*[6] 4-*tert*-butylphenol (31 g, 0.21 mol) was added to magnesium methoxide (150 g of 8 wt% solution in methanol; 12 g, 0.14 mol) and the mixture was heated to reflux. Approximately half of the methanol was distilled off and toluene (150 ml) was added to the residue. The azeotropic mixture of toluene and methanol was removed by fractional distillation until the temperature of the reaction mixture rose to 95°C. A slurry of paraformaldehyde powder (22 g, 0.73 mol) in toluene (80 ml) was added in small portions over 1 h to the reaction mixture at 95°C with concurrent removal of the methanol as by-product by distillation. Stirring was continued at 95°C for 1 hour, after which the mixture was cooled to ambient temperature. 10% sulfuric acid (220 ml) was added slowly. The resulting mixture was stirred at 30–40°C for 2 hours, after which the aqueous phase was extract with toluene (2 × 50 ml). The combined organic phase was washed with 10% sulfuric acid (30 ml) and water (30 ml). A yellow oil was obtained by evaporation under reduced and purification on silica gel using petroleum ether as eluent. Yield: 28.0 g (76%). ^1H NMR ($CDCl_3$, 400 MHz) δ in ppm 1.32 (s, 9H, ph-*tert*-butyl), 6.92 (d, J = 8.7 Hz, 1H, ph), 7.51 (d, J = 2.2 Hz, 1H, ph), 7.57 (dd, J = 8.7 and 2.2 Hz, 1H, ph), 10.82 (s, 1H, phCO-H).

2-[(Pyridyl-2-methyl)aminomethyl]-4-tert-butylphenol (**3**): The solution of 2-(aminomethyl) pyridine (1.4 g, 13.0 mmol) and **1** (2.4 g, 13.6 mmol) in 15 ml of methanol was stirred at ambient temperature for 30 min. Gas was emitted when $NaBH_4$ (0.18 g, 4.6 mmol) was added in small portion to the yellow solution at 0°C over 30 min with stirring followed by another 4 hours at ambient temperature. The resulting residue from solvent evaporation was purified on silica gel using EtOAc/EtOH (95:5) as eluent to yield 2.8 g (80%) of desired product. ^1H NMR ($CDCl_3$, 400 MHz) δ in ppm 1.26 (s, 9H, ph-*tert*-butyl), 3.94 (s, 2H, *tert*-butyl-ph-CH_2N), 4.00 (s, 2H, py-CH_2N), 6.80 (d, J = 8.4 Hz, 1H, py), 6.97 (d, J = 2.0 Hz, 1H, ph), 7.19 (d, J = 2.6 Hz, 1H, ph), 7.21 (t, J = 7.8 Hz, 1H, py), 7.24 (d, J = 7.8 Hz, 1H, py), 7.66 (td, J = 7.8 and 1.4 Hz, 1H, py), 8.58 (d, J = 4.6 Hz, 2H, py). $C_{17}H_{22}N_2O$ (270.37): calcd. C 75.52, H 8.20, N 10.36; found C 75.32, H 8.15, N 10.32.

2,6-Bis(hydroxymethyl)-4-methylphenol (**4**): Recrystallisation from EtOAc give 2.2 g (70%) of product. m.p. 127–128°C. ^1H NMR ($CDCl_3$, 400 MHz) δ in ppm 2.20 (s, 3H, ph-CH_3), 4.52 (s, 4H, ph-CH_2OH), 6.93 (s, 2H, ph-H).

2,6-Bis(chloromethyl)-4-methylphenol (**5**): Recrysallisation from hexane yield 2.1 g (68%) of product. m.p. 79–80°C. ^1H NMR ($CDCl_3$, 400 MHz) δ in ppm 2.25 (s, 3H, ph-CH_3), 4.63 (s, 4H, ph-CH_2Cl), 7.06 (s, 2H, ph-H).

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2,6-Bis{[(2-hydroxy-5-tert-butylbenzyl)(pyridyl-2-methyl)amino] methyl}-4-methylphenol (**6**): A solution of **5** (330 mg, 1.6 mmol), **3** (890 mg, 3.3 mmol) and drops of Et_3N in THF was stirred at ambient temperature for 1 hour. The solvent was evaporated. Purification on silica gel using EtOAc/MeOH (95:5) as eluent gave 0.85 g (79%) of desired product. m.p. 152–153°C. ^1H NMR ($CDCl_3$, 400 MHz) δ in ppm 1.26 (s, 18H, ph-*tert*-butyl), 2.20 (s, 3H, ph-CH_3), 3.80 (s, 4H, p-cresol-CH_2N), 3.82 (s, 4H, *tert*-butyl-ph-CH_2N), 3.88 (s, 4H, py-CH_2N), 6.76 (d, J = 8.2 Hz, 2H, py), 6.89 (s, 2H, p-cresol), 7.00 (d, J = 1.9 Hz, 2H, *tert*-butyl-ph), 7.14 (dd, J = 8.5 and 1.9 Hz, 2H, *tert*-butyl-ph), 7.20 (t, J = 6.1 Hz, 2H, py), 7.26 (d, J = 7.2 Hz, 2H, py), 7.64 (t, J = 7.8 Hz, 2H, py), 8.60 (d, J = 4.7 Hz, 2H, py). ^{13}C NMR ($CDCl_3$, 100 MHz) δ in ppm 20.61, 31.79, 34.09, 54.96, 57.19, 57.71, 116.16, 121.11, 122.60, 122.61, 123.86, 126.05, 126.89, 127.93, 131.54, 137.22, 141.82, 148.64, 154.04, 155.19, 157.18. $C_{43}H_{52}N_4O_3$ (672.90): calcd. C 76.75, H 7.79, N 8.33; found C 76.58, H 7.77, N 8.28. Electrospray ionisation mass spectrometry (ESI-MS) spectrum of **6** from CH_3OH/H_2O (85:15) gave two mono charge peaks at *m/z* 673.3 (calcd. for $[M+H]^+$, $C_{43}H_{53}N_4O_3$, 673.41) and 695.3 (calcd. for $[M+Na]^+$, $C_{43}H_{52}N_4NaO_3$, 695.39).

The complex $Mn(OAc)_3(H_2O)_2$ *with 2,6-bis{[(2-hydroxy-5-tert-butylbenzyl)(pyridyl-2-methyl)amino]methyl}-4-methylphenol* (**7**): $Mn(OAc)_3(H_2O)_2$ (122 mg, 0.45 mmol) was added to a solution of **6** (150 mg, 0.22mmol) in 3 ml $EtOH/H_2O$ (85:15). After heating at 50°C for 20 min, the mixture was cooled to ambient temperature then filtered. 1 ml of saturated NH_4PF_6 (aq.) was added to the red-brown solution whilst stirring. The mixture was kept still at 0°C for 12 hours for complete precipitation. The solid was filtered off and washed with cool methanol. 186 mg of solid was obtained after drying. Yield: 80%. $C_{47}H_{55}F_6Mn_2N_4O_7P$ (1042.80): calcd. C 54.13, H 5.32, N 5.37, Mn 10.54; found C 54.03, H 5.22, N 5.26, Mn 10.34. ESI-MS spectrum from CH_3CN gave a mono charge peaks at *m/z* 897.3 $[M\text{-}PF_6]^+$ (calcd. for $C_{47}H_{55}Mn_2N_4O_7$, 897.28); ESI-MS spectrum from CH_3OH gave two mono charge peaks of ligands exchange with methanol: (*m/z*): 869.2 $[M\text{-}CH_3COO^-+CH_3O\text{—}PF_6]^+$ (calcd. for $C_{46}H_{55}Mn_2N_4O_6$, 869.29) and 841.2 $[M\text{-}2CH_3COO^-+2CH_3O\text{—}PF_6]^+$ (calcd. for $C_{45}H_{55}Mn_2N_4O_5$, 841.29).

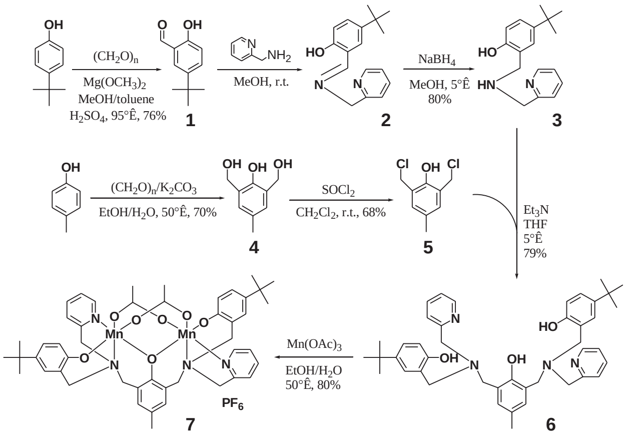
Results and discussion

The complex came from the reaction of $Mn(OAc)_3(H_2O)_2$ with the ligand as Scheme1.

NMR, IR, ESI-MS, UV/Vis and electrochemistry characterised the new ligand or complex. The exact assignment of each peak in ^1H NMR and ^{13}C NMR spectrum of ligand came from 2D-NMR (gCOSY, gHMBC, gHSQC).

IR spectra of the ligand **6** and the complex **7** were recorded between 4000 and 400 cm^{-1}. Based on characteristic frequencies and comparison with the spectrum of the ligand, the following assignments are suggested for complex **7**: 2954, 2907, 2868 cm^{-1} (m, ν C–H, aryl); 1605, 1479 cm^{-1} (m, ν C=C, aryl); 1384, 1362 cm^{-1} (w, δ C–H, aryl); 810, 760 cm^{-1} (m, γ C–H, aryl); 1577 cm^{-1} (s, ν_a C=O, carboxylate); 1430 cm^{-1} (s, ν_s C=O, carboxylate); 845 cm^{-1} (s, ν_a P–F, PF_6); 559 cm^{-1} (m, δ P–F, PF_6). 660, 592 cm^{-1} probably assigned to ν Mn–O–Mn in Mn(III,III) complex. The spectrum of **7** does not show bands at 1300 cm^{-1} (m, δ O–H) and 1111 cm^{-1} (m, ν C–O) which are seen in the spectrum of **6**, which suggested existence of phenol function proved that all phenol groups are deprotonated and coordinated to the Mn ion in the complex. $\Delta\nu = (\nu_a\ C{=}O)-(\nu_s\ C{=}O) = 147\ cm^{-1}$ indicated that two bridging acetate ligands between two Mn(III) ions were symmetrical ($\Delta\nu \geq 164\ cm^{-1}$ for asymmetrical chelating acetate ligands).[7]

The pronounced absorption at λ = 258 nm in the UV region was assigned to LC ($\pi \rightarrow \pi^*$) transition of aromatic groups.[8] The other intense absorption in the visible region (λ = 366 nm) was assigned to CT transitions from the bridging phenolate to the central Mn(III) compared with other similar phenoxo bridged Mn(III,III) complexes,[9] in which the absorption of this bridging phenolate–Mn(III) LMCT band has been observed between 320 and 400 nm. The remaining bands in the visible region might come from LMCT transitions from other ligands such as non-bridging phenolate ligands or the pyridyl ligands. LF transitions of six-coordinated Mn(III) complexes generally occur in the visible region with low intensities (typically $\varepsilon <$ 500 $M^{-1}cm^{-1}$).



Scheme 1

The electrochemical data from cyclic voltammetry in acetonitrile at v = 100 mVs^{-1} were as follows [$E_{1/2}$/V(ΔE_p/mV)]: Mn_2II,III/Mn_2II,II [–0.78 (50)], Mn_2III,III/Mn_2II,III [–0.13 (300)], Mn_2III,IV/Mn_2III,III [0.87 (60)], possible Mn_2IV,IV/ Mn_2III,IV [1.07 (90)]. No EPR signal was observed for **7**, which is interpreted as due to antiferromagnetic coupling between Mu^{II} ions. The NMR signals from **7** were too broad to allow interpretation. The structure for **7** shown in Scheme 1 is by analogy with that determined for the parent complex [Mn_2(II, II) (bpmp) (μ-$OAc)_2 \cdot PF_6$.[10]

This work was supported by the "973 program" of the Ministry of Science Technology of China and National Natural Science Foundation of China (Project 20128005).

Received 11 July 2003; accepted 1 December 2003
Paper 03/2016

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