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A novel (μ-OAc)$_2$ bridged unsymmetric coordinated binuclear Mn(II) macrocyclic complex with ligating pendant-arm

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ABSTRACT

A novel binuclear manganese Mn(II) macrocyclic complex with two pyridylmethyl pendant arms, $[Mn_2{}^{II}(H_2L)(\mu\text{-}OAc)_2](ClO_4)_2 \cdot H_2O$, has been synthesized and characterized crystallographically and magnetically. The crystal structure of the complex shows that two manganese ions locate in the same head of the macrocycle, leaving an uncoordinating cavity to catch protons through oxide of phenolate and the nearby imine groups in another head. The electrochemical study demonstrates that the complex gives two couples of redox peaks with $E_{1/2}$ of 0.3775 V and 0.8409 V, respectively. The variable temperature magnetic susceptibility measurement on the sample displays weak antiferromagnetic interaction between two manganese (II) with the $J = -3.733(7)\ \mathrm{cm}^{-1}$. This complex exhibits a moderate activity for catalyzing disproportionation of H_2O_2 to O_2.

In recent decades, the design and synthesis of mononuclear macrocyclic complexes with dinucleating ligands capable of binding two metal ions in close proximity, are of great interest, owing to their promising applications in recognizing receptors of charged ions and/or neutral small molecules [1,2], selecting cations to serve as chemical sensors [3] and molecular devices [4]. The mononuclear macrocyclic complexes have been also used in synthesizing hetero-dinuclear complexes [5,6] and mimicking catalytic activity of enzymes as host–guest complexes [7]. Although some mononuclear macrocyclic complexes and cryptates, which could recognize proton through uncoordinated site [5], were synthesized, the dinuclear macrocyclic complexes with an uncoordinating bigger cavity, which is able to catch proton in the macrocycle, are rarely produced. Here we reported this kind of novel dinuclear manganese (II) complex with pendant-arm macrocyclic Schiff base ligand in which the metals are coordinated by acetate anions and able to catch protons similar to above mentioned mononuclear complexes (Scheme 1) [9].

The X-ray single crystal diffraction analysis indicates that the title dinuclear complex contains one $[Mn_2{}^{II}(H_2L)(\mu\text{-}OAc)_2]^{2+}$, two perchlorate counter anions and one solvent water molecule [10] (Fig. 1). The structural characters of the title complex are also confirmed by its IR spectrum. The two peaks at 1591 and 1438 cm^{-1} indicate the presence of carboxylato groups. The small $\Delta\nu$ value (153 cm^{-1}) illustrates the bidentate coordination mode of carboxylato group. In addition, the characteristic vibration absorption peaks of C═N bonds in the macrocycle and ClO_4^- are observed at 1642 and 1091, 624 cm^{-1}, respectively. The structure of the title complex is quite different from previous analogous macrocyclic complexes [11]. On the one hand, two manganese ions, bridged by one phenolate oxygen and two carboxylates, are located in the half of the chamber formed by the ligand L. On the other hand, each of the imino-N atoms in other half of the chamber catches a proton similar to the previous mononuclear macrocyclic complexes [8,12], which is the first example of recognizing proton by dinuclear complex.

Selected bond lengths [Å] and angles [°]: Mn1–O1 2.134(2), Mn1–O3 2.110(2), Mn1–O5 2.203(2), Mn1–N1 2.234(2), Mn1–N3 2.383(3), Mn1–N5 2.274(2), Mn2–O1 2.092(2), Mn2–O4 2.144(2), Mn2–O6 2.116(2), Mn2–N2 2.247(2), Mn2–N4 2.322(2), Mn–N6 2.312(3), O1–Mn1–O3 102.77(8), O1–Mn1–N3 155..32(8), O3–Mn1–N3 95.88(8), O1–Mn1–N5 90.93(9), N3–Mn1–N5 73.50(9), O5–Mn1–O1 90.17(8), O5–Mn1–O3 86.00(8), O5–Mn1–N3 98.12(9), O5–Mn1–N5 84.04(9), N1–Mn1–O5 175.41(9), O1–Mn2–O6 94.32(8), O1–Mn2–N4 169.43(8), O6–Mn2–N4 94.69(9), O1–Mn2–N6 96.22(8), O6–Mn2–N6 167.86(8), N4–Mn2–N6 74.28(9), O4–Mn2–O1 98.92(7), O4–Mn2–O6 93.17(8), O4–Mn2–N4 86.08(8), O4–Mn2–N6 91.15(8), N2–Mn2–O4 177.76(9).

Each Mn(II) is coordinated with an N_3O_3 unit composed of one O_{ph}, two O_{OAc} from two 1,3-bridged acetate ions, one imine N and two N from ligating pendant-arm. The coordination configuration about Mn1 can be described as a highly distorted octahedron with O3, O5, N5, N1 in the equatorial plane (the mean deviation of

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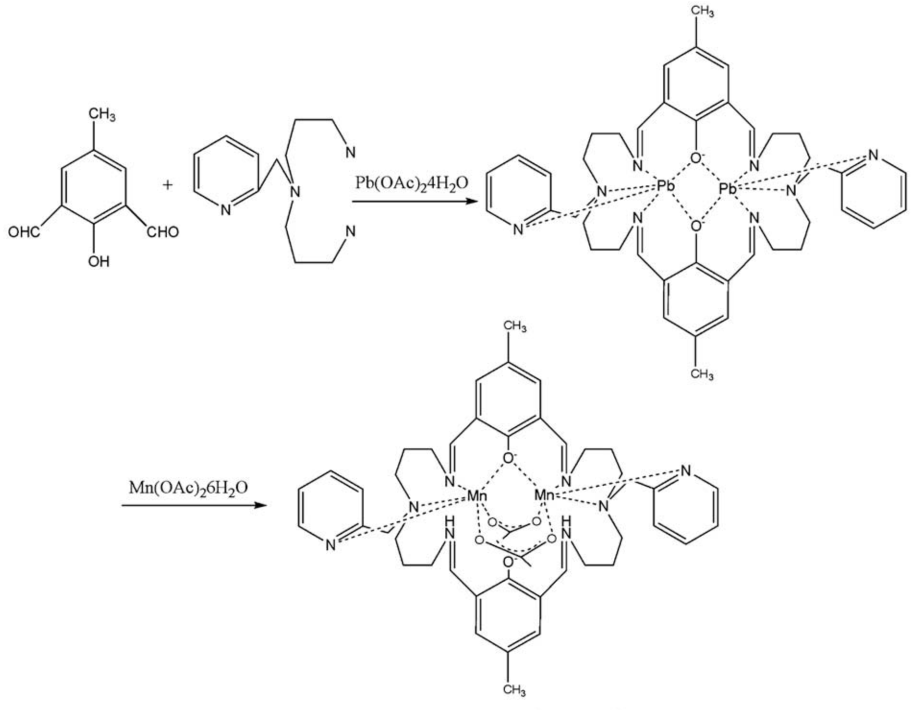

$[Mn_2H_2L^1(OAc)_2]^{2+}$

Scheme 1. The routine of the synthesis of $[Mn_2{}^{II}(H_2L)(\mu\text{-}OAc)_2](ClO_4)_2 \cdot H_2O$.

0.1232 Å) and O1, N3 in the axial sites (the bond angle of O1–Mn1–N3 is 155.3(1)°). The Mn2, for which O4, O6, N2, N6 comprise the equatorial plane (the mean deviation of 0.0873 Å) and O1, N4 occupy the axial sites (the bond angles of O4–Mn2–N2 is 177.1(1)°), respectively, exhibits more regular geometry of octahedron than that of Mn1. The Mn1···Mn2 separation is 3.401(2) Å.

The two acetate groups are asymmetrically bridging as evidenced by the $Mn–O_{OAc}$, for the Mn1–O5(2.203(2) Å) and Mn2–O4 (2.144(2) Å) distances are longer than those of the Mn1–O3 (2.110 (2) Å) and Mn2–O6 (2.116(2) Å), respectively, and the situation of the phenoxy oxygen distances are similar to above for Mn1–O1 bond (2.134(2) Å) distance is longer than that of Mn1–O2 (2.092(2) Å). The Mn–O bond length is in the usual range observed for Mn(II) complexes [13]. Two pyridine groups of pendant arms, *trans* to each other, coordinate to two metal ions with the $Mn–N_{py}$ bond lengths Mn1–N5 2.274(2) and Mn2–N6 2.312(3) Å, respectively, which are slightly longer than those of the $Mn–N_{im}$ (Mn1–N1 2.234(2) Å, Mn2–N2 2.247(2) Å). Additionally, the longest bond is the $Mn–N_{ter}$ (Mn1–N3 2.383(3) Å, Mn2–N4 2.322(2) Å). The Mn–N bond distances all fall within the range of $Mn^{II}–N$ bonds reported previously. [13,11b,c].

Elemental analysis is hard to ensure exactly number of hydrogen atoms because it is so light and X-ray determination of complexes is difficult to ascertain charges of metal ions rigorously for existence of rudimental electron. It is an effective method to explore the charges of metal ions by analyzing the magnetic interactions between metal ions in the complexes. Variable-temperature magnetic susceptibility data were recorded for the complex in the temperature range 2–300 K. No significant field dependence of the magnetic susceptibility (χ_m) was observed. The plot of χ_mT against temperature is shown in Fig. 2.

χ_mT decreases smoothly from 8.08 $cm^3\,K\,mol^{-1}$ at 300 K to 6.14 $cm^3\,K\,mol^{-1}$ at 100 K and then more abruptly to reach 0.05 $cm^3\,K\,mol^{-1}$ at 2 K. This behavior, which is very similar to that of the dimanganese(II) complex in the literature [14a], is character-

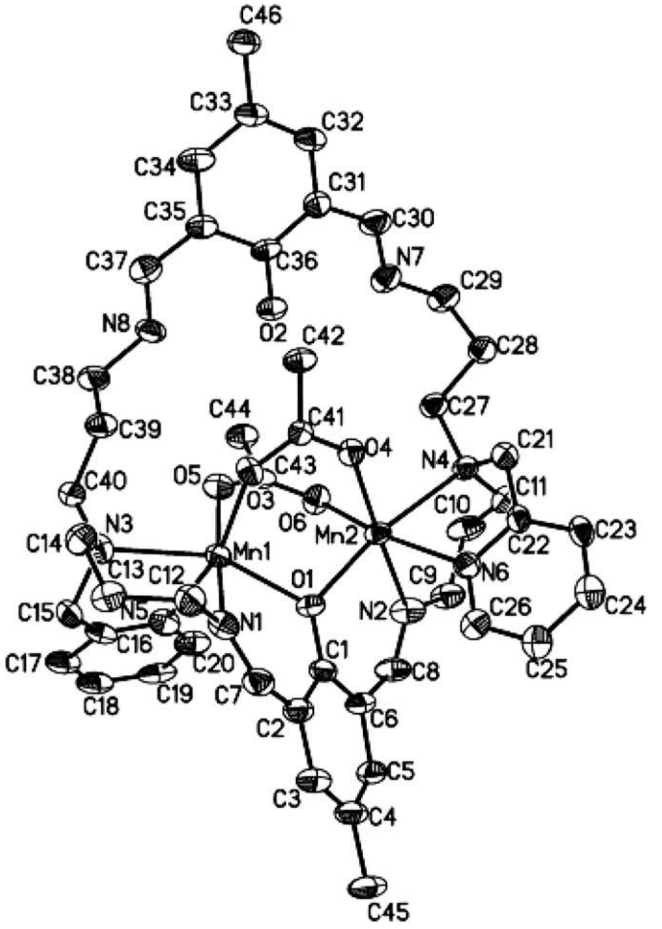

Fig. 1. Perspective view of the cation $[Mn_2{}^{II}(H_2L)(\mu\text{-}OAc)_2]^{2+}$ with thermal ellipsoids shown at 30%.

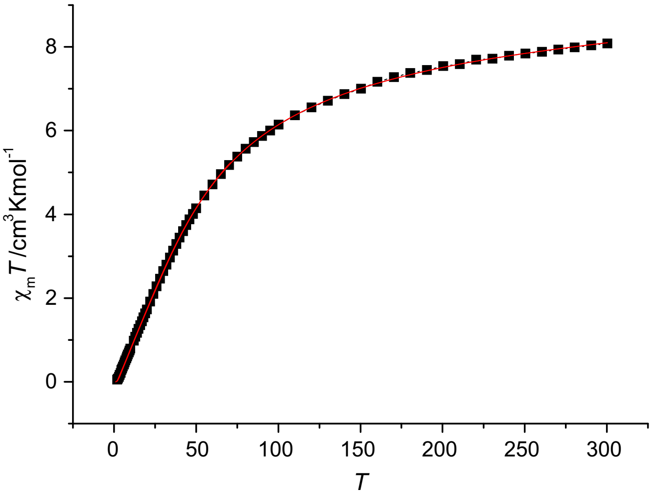

Fig. 2. Experimental and calculated plots of $\chi_m T$ vs. T. The solid line shows the fit with Eq. (1).

istic of two high-spin ($S = 5/2$) Mn(II) ions experiencing a moderate antiferromagnetic coupling. The magnetic data could be accounted for by the Van Vleck equation for two spins $S = 5/2$.

$$\chi_m = \frac{2N\beta^2 g^2}{kT}\frac{\exp(2x) + 5\exp(6x) + 14\exp(12x) + 30\exp(20x) + 55\exp(30x)}{1 + 3\exp(2x) + 5\exp(6x) + 7\exp(12x) + 9\exp(20x) + 11\exp(30x)} + 2t \tag{1}$$

where $x = J/kT$, N, g, β, k and T have their usual meanings and t is the temperature-independent paramagnetism. g was fixed to 2 in the calculations. The best least-squares fit of the experimental data were obtained with the parameters $J = -3.733(7)\ \mathrm{cm^{-1}}$, $t = 3.6(0) \times 10^{-4}\mathrm{cm^3\ mol^{-1}}$ and $R = 8.1 \times 10^{-4}$ (R is an agreement factor defined as $(\{\sum[(\chi_m T)_{\mathrm{calc}} - (\chi_m T)_{\mathrm{obs}}]^2/\sum(\chi_m T)^2_{\mathrm{obs}}\}^{1/2})$, which were agreement with the binuclear Mn(II) complexes with phenolate oxygen and 1,3-carboxylate bridging reported by previous works (range of -2 to $-10\ \mathrm{cm^{-1}}$) [14]. The experiment data in the range of 60–300 K are well approximated by a Curie–Weiss law with the values of $C = 9.727$ and $\Theta = -59.54$ K.

The results of the cyclic voltammogram experiment of the complex were also agreement with electrochemical behaviors of dimaganese (II) complexes (Fig. 3) [15]. The complex displays two quasi-reversible redox couples with the $E_{1/2}$ of 0.3775 V and 0.8409 V, respectively, which can be attributed to the redox reaction of MnIIMnII ↔ MnIIMnIII and MnIIMnIII ↔ MnIIIMnIII, respectively. The $E_{1/2}$ (1) value is similar to that of analogous $\mathrm{Mn_2^{II}L(\mu\text{-}OAc)_2}$ complex, and quite bigger than that of the mixed-value $\mathrm{Mn^{II}Mn^{III}}$ complexes (approximate to zero and even to a negative).

The CAT-like activity of $[\mathrm{Mn_2^{II}(H_2L)(\mu\text{-}OAc)_2}](\mathrm{ClO_4})_2 \cdot \mathrm{H_2O}$ to catalyze the disproportionation of H_2O_2 into H_2O and O_2 has been investigated in DMF and CH_3CN at 0 °C, respectively. The time course of the O_2-evolution by the compound is shown in Fig. 4. In DMF, the initial rate was very low, but the rate significantly increased after a lag time. The situation is similar to those of the $[\mathrm{Mn_2^{II}L^{4,4}(OAc)_2}]$ [16] and $[\mathrm{Mn_2^{II}L(PhCO_2)_2}](\mathrm{NCS})$ [17]. However, the present complex displays a longer lag time and a lower liberation of dioxygen showed by the O_2-evolution profile. The liberation of dioxygen catalyzed by$[\mathrm{Mn_2^{II}(H_2L)(\mu\text{-}OAc)_2}](\mathrm{ClO_4})_2$ (60% theoretical amount) is much lower than that catalyzed by $[\mathrm{Mn_2^{II}L^{3,3}(OAc)_2}]$ (100% theoretical amount), suggesting that the dissociation of the bridging acetates is more difficult than that of the relative ones in similar complexes [16].

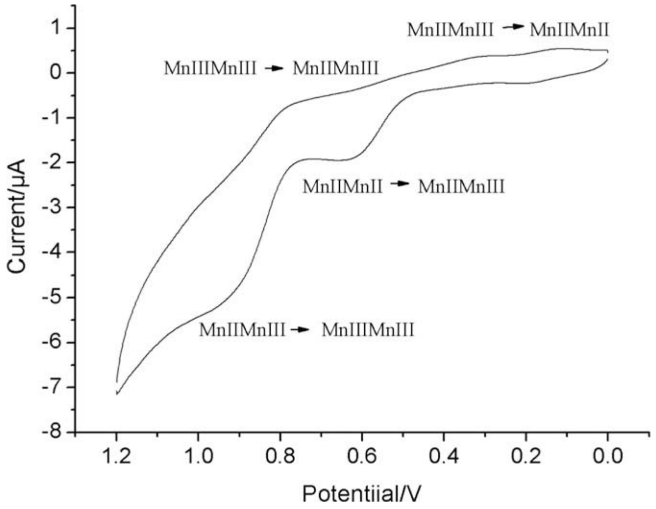

Fig. 3. Cyclic voltammogram of $[\mathrm{Mn_2^{II}(H_2L)(\mu\text{-}OAc)_2}](\mathrm{ClO_4})_2 \cdot \mathrm{H_2O}$ in DMF ($5 \times 10^{-4}\ \mathrm{mol\ L^{-1}}$) containing $0.1\ \mathrm{mol\ L^{-1}}$ $\mathrm{NBu_4ClO_4}$ on a glassy carbon electrode at a scan rate of 20 mV $\mathrm{S^{-1}}$.

For comparison, the similar experiment was carried out in CH_3CN under the same conditions; the oxygen evolution in CH_3CN was observed without lag time. The initial rate of liberation dioxygen is much lower than that of $[\mathrm{Mn_2^{II}L}](\mathrm{ClO_4})_2$[11b], but the rate significantly increased with the enhancement of the time. The percentage of disproportionation of H_2O_2 into H_2O and O_2 catalyzed by present complex is higher than that by $[\mathrm{Mn_2^{II}L}](\mathrm{ClO_4})_2$. Meanwhile, the efficiency of disproportionation of H_2O_2 catalyzed by title complex in CH_3CN is much higher than that in DMF. Furthermore, the molar conductivities of the complex in CH_3OH, DMF and CH_3CN are 400, 410 and 450 s $\mathrm{cm^2\ mol^{-1}}$, which are located in the range of 1:3 type electrolyte, and the UV spectra are slightly red shift in the order. So, the ionization of acetate coordinated to metal is

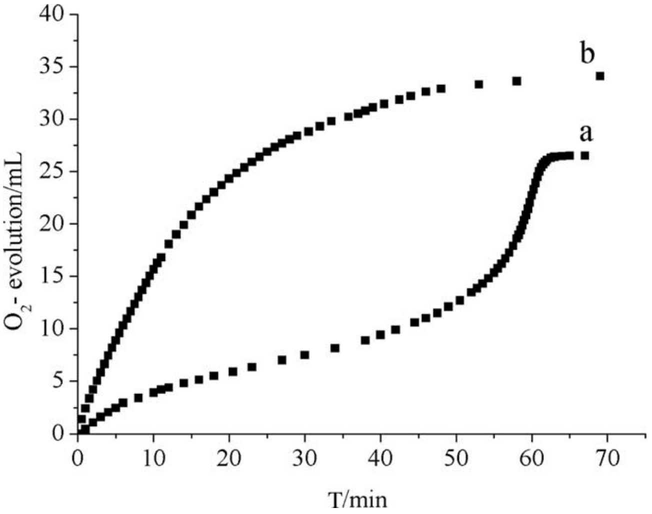

Fig. 4. Time course of O_2 evolution in the decomposition of H_2O_2 by $[\mathrm{Mn_2^{II}(H_2L)(\mu\text{-}OAc)_2}](\mathrm{ClO_4})_2$. (a) Complex 1.2 mM in DMF (2 mL); H_2O_2 6 M in DMF (0.5 mL); and (b) complex 1.2 mM in CH_3CN (2 mL); H_2O_2 6 M in CH_3CN (0.5 mL).

easier in CH_3CN solution than that in DMF solution, which is agreement with the results of CAT-like activity in the solutions.

In summary, the binuclear crystal manganese (II) complex $[Mn_2^{II}(H_2L)(\mu\text{-OAc})_2](ClO_4)_2 \cdot H_2O$ with an uncoordinating cavity caught two protons was obtained by the transmetalation reaction. The complex has the CAT-like activity in DMF and CH_3CN solution, and the efficiency of disproportionation of H_2O_2 is largely dependent on the property of solution.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.inoche.2008.09.001.

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[9] Selected IR data (ν cm^{-1} using KBr): υ_{as}(COO) 1591; υ_s (COO) 1438; υ(C=N) 1642, 1111.97; $\upsilon(ClO_4^-)$ 1091, 624. $C_{46}H_{60}Cl_2Mn_2N_8O_{15}$ (1145.8): calcd. C 48.22, H 5.28, N 9.78; found C 48.21, H 5.31, N 9.79.

[10] Diffraction intensity data were collected on a SMARTCCD area-detector diffractometer at 291 K using graphite monochromatic Mo Ka radiation ($\lambda = 0.71073$ Å). Data reduction and cell refinement were preformed by SMART and SAINT Programs. The structures were solved by direct methods (Bruker SHELXTL) and refined on F^2 by full-matrix least squares (Bruker SHELXTL) using all unique data. Crystal Data for $[Mn_2^{II}L(\mu\text{-acetato})_2](ClO_4)_2 \cdot H_2O$: $C_{46}H_{60}Mn_2N_8O_{15}Cl_2$, $M = 1145.8$. Orthorhombic, space group Pna2(1), $Z = 2$, $a = 14.414(2)$ Å, $b = 14.786(2)$ Å, $c = 15.006(2)$ Å, $\alpha = 110.372(3)°$, $\beta = 99.179(3)°$, $\gamma = 107.891(2)°$, $V = 2722.9(6)$ Å^3, $D_{caled} = 1.395$ g cm^{-3}, μ(Mo-Kα) = 0.632 mm^{-1}, $T = 291$ K. 15898 data collected, 10517 independent refections ($R_{int} = 0.0204$). Final $R_1 = 0.0481$, w$R_2 = 0.1055$ [$I > 2\sigma(I)$]. CCDC Reference Number CCDC 619821.

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