

# Synthesis, Crystal Structure and Properties of a New Trinuclear Manganese(II) Complex $\text{Mn}_3(2,2'\text{-bipy})_2(\text{C}_7\text{H}_5\text{O}_3)_6$

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A new trinuclear complex  $\text{Mn}_3(2,2'\text{-bipy})_2(\text{C}_7\text{H}_5\text{O}_3)_6$  (**1**) with  $\alpha$ -furacrylic acid (HL) and 2,2'-bipyridine as ligands has been synthesized. In **1**, six  $\text{L}^-$  anions link three Mn(II) cations to form a trinuclear structure. Each Mn cation is coordinated by six atoms to give a distorted octahedral coordination geometry. The luminescence and electrochemical properties of **1** were investigated. Complex **1** exhibits one intense fluorescence emission band at around 498 nm. It is paramagnetic showing weak antiferromagnetic coupling at low temperature. The electron transfer is irreversible in the electrode reaction of **1**, one electron being involved in the reduction corresponding to Mn(III)/Mn(II).

**Key words:** Manganese(II) Complex, Crystal Structure, Luminescence and Electrochemical Properties

## Introduction

Due to the potential applications and significant involvement in various biological systems of multinuclear manganese complexes, their molecular construction and crystal engineering have attracted much attention. There are binuclear or multinuclear manganese complexes in the active sites of Mn catalase, Mn superoxide dismutase (Mn SOD), Mn ribonucleotide reductase (Mn RR) and the oxygen-evolving complex of photosystem II in green plants [1–3]. Therefore, it is interesting to synthesize multinuclear manganese

model complexes and study their properties in order to reveal the redox process of a manganese enzyme in organisms. So far, a large number of trinuclear manganese complexes with novel structures have been reported by using different types of ligands [4–11]. Herein, we report the synthesis, crystal structure and luminescence and electrochemical properties of the new trinuclear Mn(II) complex  $\text{Mn}_3(2,2'\text{-bipy})_2(\text{C}_7\text{H}_5\text{O}_3)_6$  (**1**) with  $\alpha$ -furacrylic acid (HL) as one of the ligands.

## Results and Discussion

### Structure description

As revealed by the molecular structure (Fig. 1), **1** consists of three Mn(II) cations, six  $\text{L}^-$  anions and two 2,2'-bipyridine molecules. The ligands  $\text{L}^-$  have two coordination modes:  $\mu_2$ - $\alpha$ -furacrylato- $O, O'$  and  $\mu_2$ - $\alpha$ -furacrylato- $O, O, O'$ . They link the Mn(II) ions to give a trinuclear structure, where the end positions are coordinated by the 2,2'-bipyridine molecules. All three Mn(II) ions lie in the same line with the middle one as the center of inversion. The adjacent Mn(II)–Mn(II) distance is 3.593 Å. The coordination environment of each Mn(II) ion can be described as a distorted octahedron. Mn1 is coordinated by four oxygen atoms from three  $\text{L}^-$  lig-

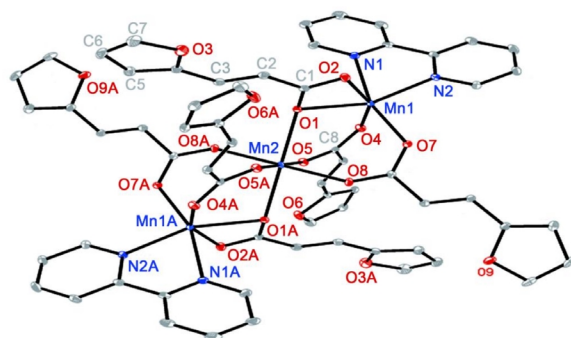


Fig. 1 (color online). Molecular structure of **1** (all hydrogen atoms are omitted for clarity). Symmetry transformation used to generate equivalent atoms:  $1-x$ ,  $1-y$ ,  $1-z$ .

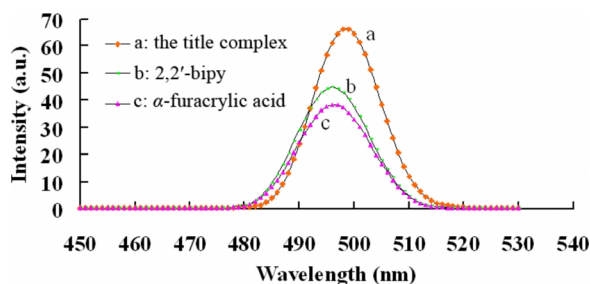


Fig. 2 (color online). Emission spectra of **1** and of the ligands in the solid state at room temperature.

ands and two nitrogen atoms from one 2,2'-bipyridine molecule. The bond angles O1–Mn1–N1, N1–Mn1–N2, N2–Mn1–O7, and O7–Mn1–O1 are 92.29(6), 71.88(6), 89.61(6), and 106.09(5)°, respectively, and their sum is 359.87°, suggesting that O1, N1, N2 and O7 are nearly lying in one plane. The Mn1–O distances vary from 2.0958(14) to 2.2649(14) Å. The average length of Mn1–N is 2.2599 Å, longer than that of Mn–N bonds (2.1525 Å) in the similar complex  $[\text{Mn}_4\text{O}_2(\text{ClCH}_2\text{COO})_7(\text{bipy})_2]\cdot\text{H}_2\text{O}$  [12]. Compared with Mn1, Mn2 is coordinated by six oxygen atoms from six  $\text{L}^-$  ligands. The bond angles O1–Mn2–O1A, O5–Mn2–O5A and O8–Mn2–O8A are all 180°. The Mn2–O distances are in the normal range of 2.1326(13)–2.2476(15) Å.

#### Luminescence properties

The fluorescence property of **1** was measured in the solid state at room temperature in the range of 400–530 nm, and the emission spectrum is shown in Fig. 2 (curve a). **1** exhibited one intense fluorescence emission band at around 498 nm with the best excitation wavelength at 500 nm. Under the same conditions, the emission bands of the free ligands 2,2'-bipyridine and HL were investigated, and they displayed fluorescence emission at about 497 nm (curve b) and 496 nm (curve c), respectively. **1** has a similar emission band shape and position compared with the ligands, which indicates that intraligand excitation is responsible for the emission of **1**. In addition, probably due to the increased rigidity of the ligands coordinated to metal ions, the fluorescence intensity of **1** is stronger than those of the ligands [13–15].

#### Electrochemical properties

Fig. 3a shows the cyclic voltammogram (CV) of **1**. In the CV measurement, we employed a conventional

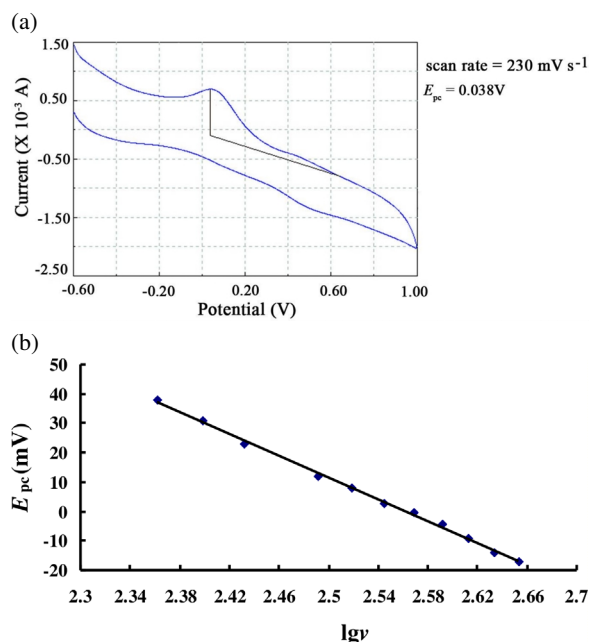


Fig. 3 (color online). (a) Cyclic voltammogram of **1** (scan rate:  $230 \text{ mV s}^{-1}$ ); (b) effect of the potential scan rate on the reduction peak potential.

three-electrode system where glass/C was chosen as the working electrode, a saturated calomel electrode (SCE) as the reference electrode, and a platinum electrode as the counter electrode. The complex was dissolved in methanol, the resulting solution having a concentration of  $1 \times 10^{-4} \text{ mol L}^{-1}$ . An HAC–NaAc solution (pH = 4.0) was used as buffer solution. The scan range was  $-0.60$  to  $1.00 \text{ V}$ , and the scan rate was  $230 \text{ mV s}^{-1}$ . The results show that there exists only one reduction peak with a peak potential of  $0.038 \text{ V}$ , demonstrating that the electron transfer in the electrode reaction is irreversible.

Under the same conditions, the influence of the potential scan rate on the reduction peak potential was studied in the range of  $230$ – $450 \text{ mV s}^{-1}$ . The reduction peak potential ( $E_{\text{pc}}$ ) shifted to a more negative value with increasing scan rate ( $v$ ), and it was proportional to  $\lg v$  in the range of  $230$ – $450 \text{ mV s}^{-1}$ . The linear regression equation was  $E_{\text{pc}} = -185.27 \lg v + 474.75 \text{ mV}$  with a correlation coefficient of  $0.9976$  (Fig. 3b). On the basis of the slope of  $E_{\text{pc}}$  with  $\lg v$ , the number of electrons involved in the reduction of **1** could be evaluated. The  $\alpha n$  was calculated to be  $0.32$ . Generally, the electron transfer coefficient  $\alpha$  is about  $0.5$  for totally irreversible electrode processes. Thus, the value of  $n$ , the electron transfer number, was

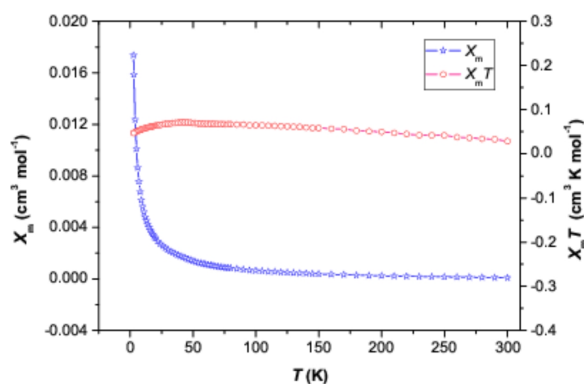


Fig. 4 (color online). Temperature dependence of the magnetic susceptibility of **1** in the form of  $\chi_M$  and  $\chi_M T$  vs.  $T$ .

about 1, indicating that one electron is involved in the reduction, and the electrode reaction corresponds to Mn(III)/Mn(II).

### Magnetic properties

The magnetic susceptibility data of **1** under variable temperatures (2.7 to 300 K) were collected with an applied magnetic field of 2 kOe. The temperature dependence of the molar magnetic susceptibility of **1** is presented in Fig. 4 in the form of  $\chi_M$  and  $\chi_M T$  vs.  $T$ . As is evident from Fig. 4, when the temperature drops to about 38 K, the value of  $\chi_M$  is significantly elevated, and the product of  $\chi_M T$  drops slowly. Such magnetic behavior indicates that **1** is a paramagnetic system and shows a weak antiferromagnetic coupling.

### Conclusion

We have synthesized a new Mn(II) complex  $\text{Mn}_3(2,2'\text{-bipy})_2(\text{C}_7\text{H}_5\text{O}_3)_6$  based on the ligand  $\alpha$ -furfuracrylic acid. The complex was characterized by X-ray diffraction analysis and fluorescence and CV measurement. The results indicate that the complex shows intense fluorescence at around 498 nm, that it is a paramagnetic system and shows a weak antiferromagnetic coupling at low temperatures, and that its electrode reaction corresponds to Mn(III)/Mn(II), the electron transfer being irreversible.

### Experimental Section

All materials were of analytical grade and used without further purification. C, H, N analysis was conducted by means of a PE-2400(II) apparatus. The melting point was determined on a Beijing-made XT4 binocular micromelt-

Table 1. Crystal structure data for **1**.

Formula	$\text{C}_{62}\text{H}_{46}\text{Mn}_3\text{N}_4\text{O}_{18}$
$M_r$	1299.85
Crystal size, $\text{mm}^3$	$0.20 \times 0.12 \times 0.08$
Crystal system	triclinic
Space group	$P\bar{1}$
$a$ , Å	11.087(2)
$b$ , Å	11.185(2)
$c$ , Å	13.012(3)
$\alpha$ , deg	65.06(3)
$\beta$ , deg	78.44(3)
$\gamma$ , deg	79.56(3)
$V$ , Å <sup>3</sup>	1424.8(5)
$Z$	1
$D_{\text{calcd}}$ , $\text{g cm}^{-3}$	1.52
$\mu(\text{MoK}\alpha)$ , $\text{cm}^{-1}$	7.4
$F(000)$ , e	665
$hkl$ range	$\pm 13, -11 \rightarrow 13, \pm 15$
$((\sin \theta)/\lambda)_{\text{max}}$ , Å <sup>-1</sup>	0.247
Refl. measured / unique / $R_{\text{int}}$	11884 / 5002 / 0.0305
Param. refined	395
$R(F) / wR(F^2)^a$ (all refl.)	0.0385 / 0.0744
A / B values (weighting scheme) <sup>a</sup>	0.430 / 0.0000
GoF ( $F^2$ ) <sup>b</sup>	1.031
$\Delta\rho_{\text{fin}}$ (max/min), $\text{e Å}^{-3}$	0.25 / -0.3

<sup>a</sup>  $R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ ;  $wR2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$ ,  $w = [\sigma^2(F_o^2) + (AP)^2 + BP]^{-1}$ , where  $P = (\text{Max}(F_o^2, 0) + 2F_c^2) / 3$ ;  
<sup>b</sup>  $\text{GoF} = [\sum w(F_o^2 - F_c^2)^2 / (n_{\text{obs}} - n_{\text{param}})]^{1/2}$ .

Table 2. Selected bond lengths (Å) and angles (deg) for **1** with estimated standard deviations in parentheses.

Mn1–O1	2.2468(13)	Mn1–N2	2.2364(16)
Mn1–O2	2.2649(14)	Mn2–O1	2.2476(15)
Mn1–O4	2.0987(14)	Mn2–O5	2.1326(13)
Mn1–O7	2.0958(14)	Mn2–O8	2.1763(14)
Mn1–N1	2.2835(16)	O7–Mn1–O2	97.64(6)
O1–Mn1–N1	92.29(6)	O4–Mn1–O1	95.13(5)
N2–Mn1–N1	71.88(6)	O4–Mn1–N1	86.59(6)
O7–Mn1–N2	89.61(6)	O4–Mn1–N2	99.81(6)
O7–Mn1–O1	106.09(5)	O7–Mn1–O4	94.71(6)
O1–Mn1–O2	58.48(5)	N2–Mn1–O1	157.37(5)
O2–Mn1–N1	89.19(6)	O7–Mn1–N1	161.36(5)
N2–Mn1–O2	104.07(6)	O4–Mn1–O2	153.09(5)

ing point apparatus. Luminescence spectra were obtained at room temperature on a WGY-10 fluorescence spectrophotometer. Cyclic voltammetry was measured on a LK98 electrochemical analysis system from Tianjin Lanlike Chemical and Electronic High-tech Co., Ltd.

### Preparation of $\text{Mn}_3(2,2'\text{-bipy})_2(\text{C}_7\text{H}_5\text{O}_3)_6$ (**1**)

A mixture of manganese acetate (0.20 mmol, 0.050 g), HL (1.01 mmol, 0.139 g) and 2,2'-bipyridine (0.17 mmol, 0.026 g) was dissolved in the mixed solvent of  $\text{CH}_3\text{CH}_2\text{OH}/\text{H}_2\text{O}$  (volume ratio 20 : 1). The pH value of the resultant mixture was adjusted to about 6.5 by adding three drops of a triethylamine solution. The mixture was heated

under water-bath conditions at about 65 °C for 20 h. The resulting solution was filtered, and the filtrate was evaporated slowly at r. t. Orange single crystals of **1** were obtained after eight weeks. M. p.: 239.5–240.0 °C. Yield: 31 %. – Anal. for  $\text{C}_{62}\text{H}_{46}\text{Mn}_3\text{N}_4\text{O}_{18}$ : calcd. C 57.29, H 3.57, N 4.31; found C 57.23, H 3.56, N 4.30.

#### X-Ray structure determination

The X-ray diffraction measurement for **1** was carried out on a Rigaku Saturn CCD area detector at  $T = 113(2)$  K by using graphite-monochromatized  $\text{MoK}\alpha$  ( $\lambda = 0.71073$  Å) radiation. The absorption correction was carried out by the program SADABS [16]. The structure was solved by Direct Methods and refined by a full-matrix least-squares technique using the programs SHELXS-97 and SHELXL-97 [17], re-

spectively. All hydrogen atoms were generated geometrically and refined isotropically using the riding model. Details of the crystal parameters, data collection and refinements are summarized in Table 1, and selected bond lengths and angles are listed in Table 2.

CCDC 829760 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

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