



# Structure, magnetic properties, catalase activity and DFT studies of $[\text{Mn}_2(\mu\text{-RCOO})_2(\mu\text{-OR})_2]^{2+}$ type dinuclear manganese(III,III) complexes

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## ABSTRACT

Three Mn(III,III) complexes containing dibenzoylmethane (dbm),  $\text{Mn}_2(\text{OMe})_2(\text{dbm})_2(\text{ClH}_2\text{CCOO})_2$  (**1**),  $\text{Mn}_2(\text{OMe})_2(\text{dbm})_2(\text{Cl}_2\text{HCCOO})_2$  (**2**) and  $\text{Mn}_2(\text{OMe})_2(\text{dbm})_2(\text{Cl}_3\text{CCOO})_2$  (**3**) were synthesized. Crystal structure determination and magnetic characterization were done for **2**. The Mn···Mn distance in complex **2** is 2.865 Å. It exhibits antiferromagnetic coupling with exchange parameter  $|J| = 20.4 \text{ cm}^{-1}$  ( $H = -2JS_A S_B$ ). All three complexes, though insoluble in common solvents, catalyse the disproportionation of hydrogen peroxide when dispersed on silica gel with turnover numbers  $\sim 150\text{--}300$ . DFT simulations showed that bridging moieties have remarkable effect on intermetallic distances in dimanganese(III,III) complexes.

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## 1. Introduction

Manganese is required in living systems to perform diverse redox functions including water splitting by photosynthetic enzymes [1–3]. The dinuclear manganese(III,III) units are present in metallo-enzymes such as Mn-catalases which are responsible for the disproportionation of hydrogen peroxide into water and oxygen and have been found in some bacteria such as *Thermus thermophilus* and *Lactobacillus plantarum* [4–6]. Besides as models for biological systems, the study of dinuclear Mn(III,III) complexes are important for probing  $d^4\text{--}d^4$  magnetic exchange coupling. A variety of Mn(III,III) complexes differing in their core units have been reported so far (Scheme 1). The core structures and observed Mn···Mn distances of oxo- and alkoxo-bridged dimanganese(III,III) complexes are as follows: Type-I,  $[\text{Mn}_2(\mu\text{-OR})_2]^{4+}$ , 3.00–3.04 Å [7–15]; Type-II,  $[\text{Mn}_2(\mu\text{-RCOO})(\mu\text{-OR})_2]^{3+}$ , 2.91–2.94 Å [16–23]; Type-III,  $[\text{Mn}_2(\mu\text{-RCOO})_2(\mu\text{-OR})_2]^{2+}$ , 2.85–2.87 Å [24–28]; Type-IV,  $[\text{Mn}_2\text{O}_2]^{2+}$ , 2.64–2.75 Å [29–36]; Type-V,  $[\text{Mn}_2(\mu\text{-RCOO})_2(\mu\text{-O})]^{2+}$ , 3.08–3.22 Å [37–48]. The first four types form complexes with coplanar equatorial planes and parallel Jahn–Teller axes, while in Type-V complexes the Jahn–Teller axes were inclined by 27–90°. Relatively few Type-III complexes have been previously reported. Here we report the synthesis, electronic spectra and catalase like activity of three Type-III complexes of dibenzoylmethane (dbm) as well as detailed crystallographic and magnetic characterization for  $\text{Mn}_2(\text{OMe})_2(\text{dbm})_2(\text{Cl}_2\text{HCCOO})_2$ . Further, geometry optimizations have been carried out using the DFT method.

## 2. Experimental

### 2.1. Materials and physical measurements

All chemicals were purchased from Ranbaxy chemicals and used without further purification.  $\text{Mn}(\text{OAc})_3 \cdot 2\text{H}_2\text{O}$  was prepared using a reported procedure [49]. IR spectra were obtained with a Shimadzu FT-IR 8000 spectrometer. Elemental analysis was obtained using a FLASH EA 1112 SERIES CHNS analyzer. Diffuse reflectance spectra were measured by using a Shimadzu UV-3100 spectrometer equipped with an ISR-3100 integrating sphere attachment. The magnetic susceptibility was measured for compound **2** in the temperature range, 2.0–300 K using a vibrating sample magnetometer (14T, VSM, PPMS-Quantum Design). Diamagnetic corrections were applied using Pascal's constants [50]. Fitting of the susceptibility data was done using the program SUSCEP [51] based on the dimer equation [52].

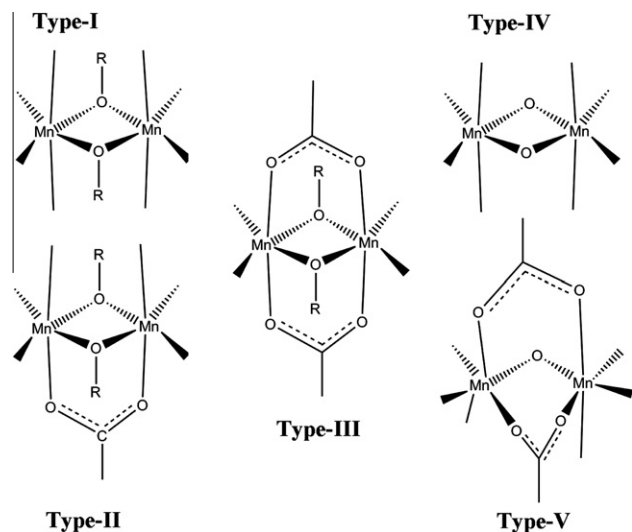
### 2.2. Synthesis

#### 2.2.1. $\text{Mn}_2(\text{OMe})_2(\text{dbm})_2(\text{ClH}_2\text{CCOO})_2$ (**1**)

Manganese(III) acetate (0.268 g, 1.00 mmol) and monochloroacetic acid (0.284 g, 3.00 mmol) were added to dichloromethane (30 mL) with constant stirring. Dibenzoylmethane (0.225 g, 1.00 mmol) was added to the above dark brown mixture, followed by 5 mL of methanol. The resulting dark brown solution was filtered immediately and layered with diethyl ether and kept at 5 °C. A microcrystalline precipitate was obtained within 2 days which was collected by filtration. Yield 0.266 g (0.33 mmol, 66%). Anal. Calc. for  $\text{Mn}_2\text{C}_{36}\text{H}_{32}\text{Cl}_2\text{O}_{10}$  (M.W. 805.41): C, 53.68, H, 4.00. Found: C, 53.75; H, 3.91%. Important IR absorptions (KBr disk,

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Scheme 1. Types of oxo- and alkoxo-bridged manganese(III,III) dimeric cores.

$\text{cm}^{-1}$ ): 3057, 2924, 1707, 1686, 1632, 1589, 1518, 1480, 1381, 1337, 1248, 1069, 1022, 939, 787, 725, 687, 629, 571 and 465.

#### 2.2.2. $\text{Mn}_2(\text{OMe})_2(\text{dbm})_2(\text{Cl}_2\text{HCCOO})_2$ (**2**)

The procedure was identical to that adopted for compound **1**, except for the use of dichloroacetic acid (0.246 mL, 3.00 mmol). In this case, small dark brown needle shaped crystals were formed. Yield 0.273 g (0.31 mmol, 62%). *Anal. Calc.* for  $\text{Mn}_2\text{C}_{36}\text{H}_{30}\text{Cl}_4\text{O}_{10}$  (M.W. 874.28): C, 49.45, H, 3.46. Found: C, 49.83; H, 3.24%. Important IR absorptions (KBr disk,  $\text{cm}^{-1}$ ): 3059, 2924, 1628, 1587, 1516, 1487, 1437, 1361, 1321, 1219, 1161, 1120, 1097, 1068, 1043, 1024, 941, 825, 769, 713, 679, 596, 551 and 478.

#### 2.2.3. $\text{Mn}_2(\text{OMe})_2(\text{dbm})_2(\text{Cl}_3\text{CCOO})_2$ (**3**)

The procedure was identical to that adopted for compound **1**, except for the use of trichloroacetic acid (0.500 g, 3.06 mmol). A microcrystalline precipitate was obtained within 1 day. Yield 0.221 g (0.23 mmol, 47%). *Anal. Calc.* for  $\text{Mn}_2\text{C}_{36}\text{H}_{28}\text{Cl}_6\text{O}_{10}$  (M.W. 943.19): C, 45.84, H, 2.99. Found: C, 45.43; H, 2.82%. Important IR absorptions (KBr disk,  $\text{cm}^{-1}$ ): 3059, 2957, 2924, 2822, 1651, 1602, 1588, 1514, 1487, 1435, 1325, 1229, 1186, 1159, 1121, 1071, 1044, 1024, 941, 833, 770, 741, 714, 700, 681, 596, 552 and 461.

#### 2.2.4. Preparation of complex doped aero gel for hydrogen peroxide disproportionation

Alkoxide solution was prepared by mixing 5.0 mL of tetraethoxysilane with 11 mL of ethanol. To this was added the catalyst solution which was a mixture of 7 mL water, 11 mL ethanol and 0.37 mL ammonium fluoride/ammonium hydroxide stock solution (prepared by dissolving 1.852 g of  $\text{NH}_4\text{F}$  in 100 mL of water and adding 22.78 mL of 30% ammonium hydroxide solution). Immediately, 0.203 g of complex **1** was added and stirred until it became viscous and kept aside for gel formation. Gel was formed within 2 min and it was kept undisturbed for 1 day. The gel was aged for 1 day with 1:1 ethanol–water mixture and washed with 2 mL of ethanol. The processed gel was kept for evaporation at 60–80 °C on a water bath till constant weight was achieved. After drying, the weight of the aero gel was 1.378 g. The same procedure was repeated for complexes **2** and **3** by adding 0.203 g of respective complexes. The weights of prepared aero gels were 1.476 g for **2** and 1.394 g for **3**.

For studying the catalytic disproportionation of hydrogen peroxide, 10–12 mg of the above gel was added to 5 mL of 30% hydrogen peroxide in a flask and the volume of oxygen evolved was measured using a gas burette for several hours. A simultaneous blank experiment was conducted with undoped silica gel under the same conditions, but no gas evolution was observed.

#### 2.3. X-ray crystallography

Data were collected for a needle shaped crystal of compound **2** on a Bruker SMART APEX CCD X-ray diffractometer using graphite monochromated  $\text{Mo K}\alpha$  radiation. The data was reduced using SAINTPLUS [53], and multiscan absorption correction using SADABS [54] was applied. The structure was solved using SHELXS-97 and refined using SHELXL-97 [55]. All ring hydrogen atoms were assigned on the basis of geometrical considerations and were allowed to ride upon the respective carbon atoms. The chlorine atoms Cl1 and Cl2 were disordered on two positions. The atom Cl1 with occupancy (%) 69 and 31 and the atom Cl2 with occupancy (%) 53 and 47 were assigned directly from the Fourier peaks. The chlorine atoms with highest occupancy were used for the drawings. Crystal data are in Table 1, and important interatomic distances and angles are in Table 2.

#### 2.4. Theoretical calculations

DFT calculations were done by using the B3LYP exchange correlation functional [56] as implemented in the GAUSSIAN-03 [57] program suite. The spin-unrestricted version was employed for open shell ions. The basis set, 6-31G\*\* was used for all atoms.

### 3. Results and discussion

#### 3.1. Synthesis and spectra

The compounds **1**, **2** and **3** were synthesized by using a similar procedure starting with Mn(III) acetate in methanol–dichloromethane medium. Only compound **2** could be obtained in the form of X-ray quality crystals by the layering technique. The compounds are insoluble in common organic solvents. The crystal structure of **2** (vide supra) reveals a dinuclear complex in which octahedrally coordinated Mn(III) ions are chelated by a dbm ligand and bridged

Table 1  
Crystallographic data for **2**.

| Formula   | $\text{Mn}_2\text{C}_{36}\text{H}_{30}\text{Cl}_4\text{O}_{10}$ |
|---|---|
| Formula weight  | 874.28  |
| Crystal system  | monoclinic  |
| Space group   | $P2_1/c$  |
| <i>a</i> (Å)  | 9.922(3)  |
| <i>b</i> (Å)  | 20.265(6)   |
| <i>c</i> (Å)  | 9.539(3)  |
| $\beta$ (°)   | 101.247(5)  |
| <i>V</i> (Å <sup>3</sup> )                                  | 1881.2(10)  |
| <i>Z</i>  | 2   |
| <i>T</i> (°C)   | 100(2)  |
| <i>D</i> <sub>calc</sub> (g cm <sup>-3</sup> )              | 1.543   |
| $\mu$ (mm <sup>-1</sup> )                                   | 1.011   |
| <i>F</i> (0 0 0)  | 888   |
| Crystal size (mm)   | 0.22 × 0.10 × 0.08  |
| $\theta$ Range (°)  | 2.01–25.00  |
| <i>h</i> / <i>k</i> / <i>l</i>                              | –11, 11/–24, 24/–11, 11   |
| Reflection collected  | 17 811  |
| Unique reflections ( <i>R</i> <sub>int</sub> )              | 3303 (0.0602)   |
| Goodness-of-fit (GOF) on <i>F</i> <sup>2</sup>              | 1.053   |
| <i>R</i> <sub>1</sub> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] | 0.0570  |
| <i>wR</i> <sub>2</sub> (all data)                           | 0.1280  |

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