



Synthesis, crystal structure and magnetic properties of new dinuclear Mn(III) compounds with 4-ClC₆H₄COO and 4-BrC₆H₄COO bridges

Montserrat Corbella^{a,*}, Veronica Gómez^a, Beltzane Garcia^a, Elisenda Rodriguez^a, Belen Albela^a, Miguel A. Maestro^b

^a Departament de Química Inorgànica, Universitat de Barcelona, Martí i Franquès 1-11, 08028 Barcelona, Spain

^b Departamento de Química Fundamental, Universidade da Coruña, 15071-A Coruña, Spain

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ABSTRACT

Four new dinuclear Mn(III) compounds have been synthesised: $[\{\text{Mn}(\text{bpy})(\text{H}_2\text{O})\}_2(\mu\text{-4-ClC}_6\text{H}_4\text{COO})_2(\mu\text{-O})](\text{ClO}_4)_2$ (**1**), $[\{\text{Mn}(\text{EtOH})(\text{phen})\}_2(\mu\text{-O})(\mu\text{-4-ClC}_6\text{H}_4\text{COO})_2](\text{ClO}_4)_2$ (**2**), $[\{\text{Mn}(\text{bpy})(\text{EtOH})\}_2(\mu\text{-4-BrC}_6\text{H}_4\text{COO})_2(\mu\text{-O})](\text{ClO}_4)_2$ (**3**) and $[\{\text{Mn}(\text{H}_2\text{O})(\text{phen})\}_2(\mu\text{-4-BrC}_6\text{H}_4\text{COO})_2(\mu\text{-O})](\text{ClO}_4)_2$ (**4**). The crystal structures of **2** and **3** are evidence for the tendency of the ethanol and the perchlorate to act as ligands. Due to the coordination of these groups, the environment of the manganese ions is elongated in the monodentate ligand direction, and this distortion is more important when this ligand is the perchlorate. The magnetic properties of the four compounds have been analysed: compounds **1**, **3** and **4** show antiferromagnetic behaviour, with $J = -6.33 \text{ cm}^{-1}$ for **1**, $J = -6.76 \text{ cm}^{-1}$ for **3** and $J = -3.08 \text{ cm}^{-1}$ for **4** ($H = -JS_1 \cdot S_2$), while compound **2** shows a very weak ferromagnetic coupling. For this compound, at low temperature the most important effect on the χ_{MT} data is the zero-field splitting of the ion, and the best fit was obtained with $|D_{\text{Mn}}| = 2.38 \text{ cm}^{-1}$ and $|E_{\text{Mn}}| = 0.22 \text{ cm}^{-1}$.

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1. Introduction

Interest in dinuclear Mn(III) complexes with carboxylate ligands is due to their presence in some metalloenzymes, such as Mn-catalase, an antioxidant enzyme that catalyse the disproportionation of the H₂O₂ [1]. With the aim of obtaining good model compounds of this enzyme, several dinuclear Mn(III) complexes with a $[\text{Mn}_2(\mu\text{-O})(\mu\text{-RCOO})_2]^{2+}$ core have been reported in the literature [2–14], and in some cases, they are magnetically and structurally characterized [3–14]. Despite the magnetic interaction for this kind of compound is weak, the interest lies in the versatility of its magnetic behaviour and its relationship with the distortion of the coordination polyhedra.

Due to the Jahn–Teller effect, the Mn(III) environment is always distorted, but the kind and degree of distortion depends on the external ligands that complete the hexacoordination. Tridentate ligands usually induce a compressed distortion in the oxo-bridge direction [3], while if the blocking ligand is bidentate, the presence of a monodentate ligand to complete the coordination of the Mn(III) ion is necessary. This means that the environment is more flexible and the coordination polyhedra could be elongated, rhombic or an intermediate situation.

Some magneto-structural studies were reported in the literature for this kind of compound [4,6,8] and show that, in general, compounds with an octahedron compressed in the direction of the oxo-bridge show ferromagnetic coupling, while complexes with an elongated octahedron (*z* axis) show antiferromagnetic coupling (Scheme 1). When the distortion is rhombic, the magnetic interaction can be either ferro- or antiferromagnetic. In agreement with these studies, the magnetic interaction of the compounds with formula $[\{\text{Mn}(\text{NN})(\text{L})\}_2(\mu\text{-O})(\mu\text{-RCOO})_2]\text{X}_2$ could be ferro- or antiferromagnetic [5–14].

As continuation of the magneto-structural studies of this kind of dinuclear complexes, we report four new compounds with 4-halobenzoate bridges and 2,2'-bipyridine (bpy) or 1,10-phenanthroline (phen) as blocking ligands: $[\{\text{Mn}(\text{bpy})(\text{H}_2\text{O})\}_2(\mu\text{-4-ClC}_6\text{H}_4\text{COO})_2(\mu\text{-O})](\text{ClO}_4)_2$ (**1**), $[\{\text{Mn}(\text{EtOH})(\text{phen})\}_2(\mu\text{-O})(\mu\text{-4-ClC}_6\text{H}_4\text{COO})_2](\text{ClO}_4)_2 \cdot 3 \text{ EtOH}$ (**2**), $[\{\text{Mn}(\text{bpy})(\text{EtOH})\}_2(\mu\text{-4-BrC}_6\text{H}_4\text{COO})_2(\mu\text{-O})](\text{ClO}_4)_2 \cdot 0.33 \text{ MeCN}$ (**3**) and $[\{\text{Mn}(\text{H}_2\text{O})(\text{phen})\}_2(\mu\text{-4-BrC}_6\text{H}_4\text{COO})_2(\mu\text{-O})](\text{ClO}_4)_2$ (**4**). Compounds **2** and **3** have been characterized by X-ray diffraction, and the magnetic study of the four compounds has been carried out.

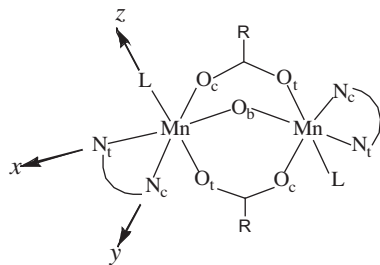
2. Experimental

2.1. Synthesis

All manipulations were performed in aerobic conditions. Organic reagents were used as received. NBu_4MnO_4 was prepared as de-

* Corresponding author.

E-mail addresses: montse.corbella@qi.ub.es, montse.corbella@ub.edu (M. Corbella).



Scheme 1. Schematic structure of the dinuclear Mn(III) complexes, with the distortion axes of the octahedron.

scribed in the literature [15]. Yield was calculated from total available Mn. *Caution!* Perchlorate salts of compounds containing organic ligands are potentially explosive. Only small quantities of these compounds should be prepared and handled behind suitable protective shields.

2.1.1. $\{[Mn(bpy)(H_2O)]_2(\mu-4-ClC_6H_4COO)_2(\mu-O)\}(ClO_4)_2$ (**1**)

1.6 mmol (0.25 g) of 4-ClC₆H₄COOH was added to a solution containing 1.28 mmol (0.46 g) of Mn(ClO₄)₂·6H₂O in 25 mL of EtOH. Then, 0.32 mmol of NBu₄MnO₄ (0.11 g) dissolved in 20 mL of EtOH was added to the solution, which immediately turned dark brown. Finally, 1.6 mmol (0.25 g) of 2,2'-bipyridine was added. The resulting dark red-brown solution was stirred for 30 min and filtered to remove a beige precipitate. Layering the filtrate with hexanes (50 mL) and storage at ca. 10 °C for several days gave rise to dark red-purple microcrystals. These were collected by filtration, washed in ether and dried in air. The yield was 25% (0.26 g). *Anal.* Calc. for C₃₄H₂₈N₄O₁₅Cl₄Mn₂EtOH: C, 41.96; H, 3.33; N, 5.44; Cl, 13.76. Found: C, 42.8; H, 3.3; N, 5.5; Cl, 13.5%. FT-IR data (KBr, main bands, cm⁻¹): 1594 (s), 1556 (s), 1498 (m), 1470 (m), 1447 (s), 1402 (s), 1372 (vs), 1171 (m), 1114 (vs), 1089 (vs), 1057 (s), 1033 (s), 1013 (s), 772 (s), 730 (s), 664 (w), 653 (w), 625 (m), 544 (w), 413 (w). $\Lambda_M = 322 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$.

2.1.2. $\{[Mn(EtOH)(phen)]_2(\mu-O)(\mu-4-ClC_6H_4COO)_2\}(ClO_4)_2$ (**2**)

1.6 mmol (0.25 g) of 4-ClC₆H₄COOH was added to a solution containing 1.28 mmol (0.46 g) of Mn(ClO₄)₂·6H₂O in 20 mL of EtOH. Then, 0.32 mmol (0.11 g) of NBu₄MnO₄ dissolved in 15 mL of EtOH was added to the solution, which immediately turned dark brown. Finally, a solution of 1.6 mmol (0.32 g) of 1,10-phenanthroline (in 5 mL of EtOH) was added. The resulting solution was stirred for 15 min and the brown precipitate formed was removed by filtration. The solution was left undisturbed at 10 °C and suitable crystals for X-ray diffraction were obtained by slow evaporation. The yield of the desired crystalline product was 14% (0.12 g). *Anal.* Calc. for C₄₂H₃₆Cl₄Mn₂N₄O₁₅: C, 46.35; H, 3.33; N, 5.15; Cl, 13.03. Found: C, 45.9; H, 3.3; N, 5.2; Cl, 13.1%. FT-IR data (KBr, main bands, cm⁻¹): 1593 (s), 1556 (m), 1518 (m), 1426 (m), 1401 (s), 1381 (s), 1120 (vs), 1108 (vs), 1089 (vs), 875 (vs), 849 (m), 772 (m), 721 (s), 625 (s). $\Lambda_M = 359 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$.

2.1.3. $\{[Mn(bpy)(EtOH)](\mu-4-BrC_6H_4COO)_2(\mu-O)\}(Mn(bpy)(ClO_4))(ClO_4)$ (**3**)

A solution of 1.6 mmol (0.32 g) of 4-BrC₆H₄COOH in 20 mL of EtOH was added to a solution containing 1.28 mmol (0.46 g) of Mn(ClO₄)₂·6H₂O in 5 mL of MeCN. Then, 0.32 mmol (0.11 g) of NBu₄MnO₄ dissolved in 10 mL of MeCN was added to the solution, which immediately turned dark brown. Finally, a solution of 1.6 mmol (0.25 g) of 2,2'-bipyridine in 5 mL of MeCN was added. The resulting dark brown solution was stirred for 10 min, filtered to remove some precipitate and 15 mL of hexanes were added.

The mixture was kept undisturbed at -5 °C; after a week dark crystals of the product were obtained, some of them suitable for X-ray diffraction. The yield was 50% (0.55 g). *Anal.* Calc. for C₃₆H₃₀N₄O₁₄Br₂Cl₂Mn₂·0.5MeCN: C, 40.26; H, 2.88; N, 5.71. Found: C, 40.1; H, 3.0; N, 5.5%. FT-IR data (KBr, main bands, cm⁻¹): 1597 (s), 1558 (s), 1493 (m), 1478 (m), 1449 (s), 1400 (s), 1381 (vs), 1104 (vs), 933 (w), 841(w), 768 (vs), 729 (s), 630 (s), 511 (m). $\Lambda_M = 275 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$.

2.1.4. $\{[Mn(H_2O)(phen)]_2(\mu-4-BrC_6H_4COO)_2(\mu-O)\}(ClO_4)_2$ (**4**)

A solution of 1.6 mmol (0.32 g) of 4-BrC₆H₄COOH in 20 mL of EtOH was added to a solution containing 1.28 mmol (0.46 g) of Mn(ClO₄)₂·6H₂O in 5 mL of MeCN. Then, 0.32 mmol (0.11 g) of NBu₄MnO₄ dissolved in 10 mL of MeCN was added to the solution, which immediately turned dark brown. Then, a solution of 1.6 mmol (0.32 g) of 1,10-phenanthroline in 5 mL of MeCN was added and finally 1.6 mmol (0.56 g) of NaClO₄·H₂O in 5 mL of MeCN. The resulting dark brown solution was stirred for 10 min, filtered to remove some precipitate and kept undisturbed at -5 °C. After a week dark crystals of the product were obtained. X-ray diffraction has confirmed the presence of the dinuclear complex, but the quality of the crystals was not good and it was not possible to resolve the crystalline structure. The yield was 21% (0.38 g). *Anal.* Calc. for C₃₈H₂₈N₄O₁₅Br₂Cl₂Mn₂: C, 40.71; H, 2.52; N, 5.00. Found: C, 40.6; H, 2.5; N, 4.8%. FT-IR data (KBr, main bands, cm⁻¹): 1589 (vs), 1555 (m), 1519 (m), 1427 (m), 1400 (vs), 1384 (vs), 1342 (m), 1110 (vs), 1010 (m), 875 (w), 849 (m), 767 (m), 720 (s), 623 (m), 5061 (w), 431 (w). $\Lambda_M = 211 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$.

2.2. Physical measurements

Analyses of C, H, N and Cl were carried out by the "Servei de Microanàlisi" of the "Consell Superior d'Investigacions Científiques (CSIC)". Infrared spectra were recorded on KBr pellets, in the range 4000–400 cm⁻¹, with a Termo Nicolet Avatar 330 FT-IR spectrometer. Conductivity measurements of 10⁻³ M acetonitrile solutions were carried out with a HACH HQ40d sensor at room temperature. Magnetic susceptibility measurements between 4–300 K, for compounds **1** and **3**, were carried out with a MANICS-DSM8 susceptometer equipped with an Oxford Instrument liquid helium cryostat, at the "Unitat de Mesures Magnètiques (Universitat de Barcelona)". For compounds **2** and **4**, the magnetic susceptibility measurements between 2–300 K and magnetization measurements (for compound **2**), at 2 K, between 0–5 T and in the 1.8–6.8 K and 0.5–5 T range, were carried out in a Quantum Design MPMP SQUID Magnetometer at the "Unitat de Mesures Magnètiques (Universitat de Barcelona)". Pascal's constants were used to estimate the diamagnetic corrections for the compounds. The fit was performed by minimising the function $R = \sum[(\chi_M T)_{\text{exp}} - (\chi_M T)_{\text{calc}}]^2 / \sum(\chi_M T)_{\text{exp}}^2$.

2.3. Crystallographic measurements

X-ray diffraction measurements and resolution of compound **2** were carried out at the "Unidade de Raios X (Universidade de Santiago de Compostela)" while compound **3** was elucidated at the "Servicios Xerais de Apoio a Investigación (Universidade da Coruña)". Crystals of **2** and **3**, obtained as described in the experimental section, were mounted onto a sealed tube and X-ray crystallographic data were collected at 100 and 298 K, respectively. The measurements of **2** were made on a Bruker Kappa APEXII CCD diffractometer and the measurements of **3** on a Bruker SMART-CCD area diffractometer, with graphite monochromated Mo K α radiation ($\lambda = 0.7107 \text{ \AA}$). The structures were solved using the SIR97 program [16] (compound **2**) or the SHELXS program [17] (compound **3**) and refined by full-matrix least-squares method using the SHELXL97

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