



Synthesis, structural characterization and magnetic properties of mixed-valent bis-bipyridine manganese carboxylate clusters

E. Carolina Sañudo^a, Vincent A. Grillo^a, Jae Yoo^b, John C. Huffman^a,
John C. Bollinger^a, David N. Hendrickson^{* b,1}, George Christou^{* a,2}

^a Department of Chemistry, Indiana University, Bloomington, IN 47405-4001, USA

^b Department of Chemistry, University of California at San Diego, La Jolla, CA 92093-4001, USA

Received 17 September 2000; accepted 28 October 2000

Abstract

Procedures have been developed for the synthesis of complexes containing the cations $[\text{Mn}_4\text{O}_2(\text{O}_2\text{CR})_4(\text{L})_2]^{2+}$ ($\text{R} = \text{Me}, \text{Et}, \text{Ph}$) (**1**) and $[\text{Mn}_4\text{O}_2(\text{MeO})_3(\text{O}_2\text{CPh})_2(\text{L})_2(\text{MeOH})]^{2+}$ (**2**). Treatment of the corresponding $[\text{Mn}_3\text{O}(\text{O}_2\text{CR})_6(\text{py})_3](\text{ClO}_4)$ complex with the ligand 1,2-bis(bipyridine-6'-yl)ethane (L) in MeCN or MeOH leads to the formation of **1** and **2**, respectively. Both complexes contain $[\text{Mn}_4\text{O}_2]$ cores. Complex **1** has overall antiferromagnetic coupling resulting in a $S = 1$ spin ground state. The metal centers in the core of complex **2** are also antiferromagnetically coupled, but in this case the spin ground state is $S = 7/2$. Complex **2** also displays an out of phase signal in the ac magnetic susceptibility study, indicating it to be a new example of single molecule magnet (SMM). © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Manganese; Tetranuclear complexes; 1,2-Bis(bipyridine-6'-yl)ethane; Single molecule magnets; Photosystem II

1. Introduction

Manganese has many available oxidation states that can coexist in mixed-valence complexes giving rise to interesting chemical and magnetic properties. Ferromagnetic or antiferromagnetic interactions among the different manganese centers of a cluster can give rise to high spin species, some of which are single molecule magnets (SMM) [1]. These molecules possess a high spin ground state with large magnetic anisotropy and they show out-of-phase ac magnetic susceptibility signals. Mn is also a biologically relevant metal, appearing in nature in the water oxidation complex (WOC) of photosystem II (PSII) [2], among others. In PSII, the tetranuclear Mn cluster of an as yet unknown structure is responsible for oxidizing H_2O to O_2 .

The ligand 1,2-bis(bipyridine-6'-yl)ethane (L) [3] has previously been used in our group to obtain high nuclearity iron and cobalt complexes [4]. In the present

work, the ligand L has been employed in Mn chemistry to obtain new manganese clusters. Special emphasis will be devoted to the complexes $[\text{Mn}_4\text{O}_2(\text{O}_2\text{CET})_4(\text{L})_2](\text{ClO}_4)_2$ (**1**) and $[\text{Mn}_4\text{O}_2(\text{MeO})_3(\text{O}_2\text{CPh})_2(\text{L})_2(\text{MeOH})](\text{ClO}_4)_2$ (**2**) and the study of their magnetic properties.

2. Experimental

2.1. Syntheses

Treatment of the corresponding $[\text{Mn}_3\text{O}(\text{O}_2\text{CR})_6(\text{py})_3](\text{ClO}_4)$ complex with 1.5 equiv. of the ligand 1,2-bis(bipyridine-6'-yl)ethane (L) in MeCN or MeOH leads to the formation of $[\text{Mn}_4\text{O}_2(\text{O}_2\text{CR})_4(\text{L})_2](\text{ClO}_4)_2$ (**1**) and $[\text{Mn}_4\text{O}_2(\text{MeO})_3(\text{O}_2\text{CPh})_2(\text{L})_2(\text{MeOH})](\text{ClO}_4)_2$ (**2**), respectively. Crystals suitable for X-ray crystallography can be obtained by slow diffusion of THF into an MeCN solution of **1**, and upon cooling a hot MeOH solution of **2**. Complexes **1** and **2** can be interconverted by dissolving **1** in MeOH or by adding carboxylate to a solution of **2**. The products have been characterized by

¹ *Corresponding author.

² *Corresponding author. Tel./fax: +1-812-855-2399; e-mail: christou@indiana.edu.

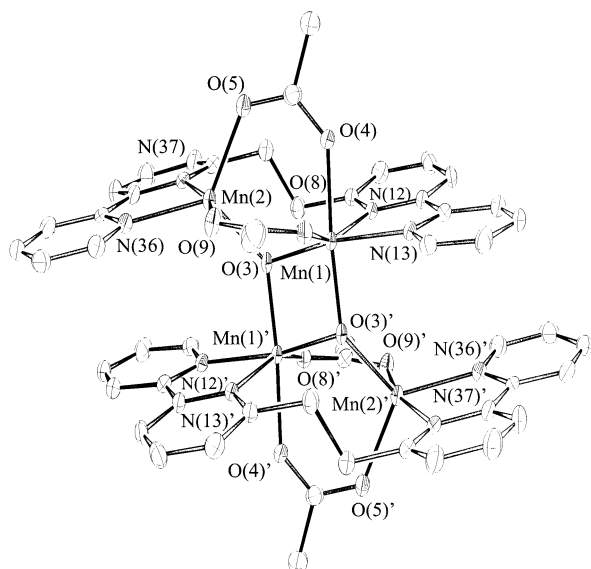


Fig. 1. ORTEP plot at the 50% probability level of the cation $[\text{Mn}_4\text{O}_2(\text{O}_2\text{CMe})_4(\text{L})_2]^{2+}$ (**1**).

IR, ^1H NMR, elemental analysis and X-ray crystallography. Full experimental details will be provided in the full paper [5].

2.2. Physical measurements

Dc and ac magnetic-susceptibility data were collected on powdered microcrystalline samples (restrained in

icosane to prevent torquing) on a Quantum Design SQUID magnetometer equipped with a 5.5 T (55 kG) magnet for **1** and a 7 T (70 kG) magnet for **2**. A diamagnetic correction to the observed magnetic susceptibilities was applied using Pascal's constants.

3. Results and discussion

3.1. Description of structures

The structure of the cation of **1** (Fig. 1) consists of two $[\text{Mn}_2\text{O}(\text{O}_2\text{CMe})_2(\text{L})]^+$ fragments held together by interfragment linkages $\text{Mn}(1)–\text{O}(3')$ and $\text{Mn}(1')–\text{O}(3)$. The cation is centrosymmetric and mixed-valent (2Mn(II), 2Mn(III)) and, on the basis of the structural parameters, the Mn(II) and Mn(III) centers are penta-coordinate Mn(2) and hexacoordinate Mn(1), respectively. Each resulting Mn(II)–Mn(III) pair is quadruply bridged by O(3), two *syn, syn*- MeCO_2^- groups, and the L ligand, which is attached to both metals. Interestingly, all bipyridine rings are essentially parallel, providing additional interfragment interactions by π stacking. Intermolecular π stacking also exists.

The structure of the cation of **2** (Fig. 2) consists of a ladder-like $[\text{Mn}_4\text{O}_4]$ core, with two of the oxygen atoms being part of bridging methoxide groups. The cation does not have any crystallographic symmetry and it is mixed valent (Mn(II), 3Mn(III)). On the basis of the structural parameters, the Mn(II) centers can be

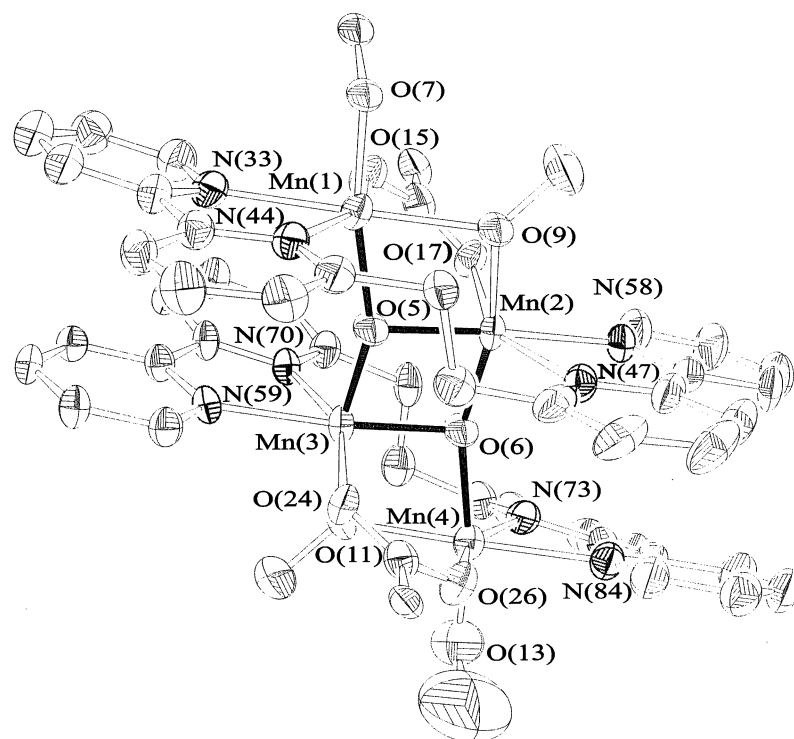


Fig. 2. ORTEP plot at the 50% probability level of the cation $[\text{Mn}_4\text{O}_2(\text{MeO})_3(\text{O}_2\text{CPh})_2(\text{L})_2(\text{MeOH})]^{2+}$ (**2**). The phenyl rings are omitted for clarity.

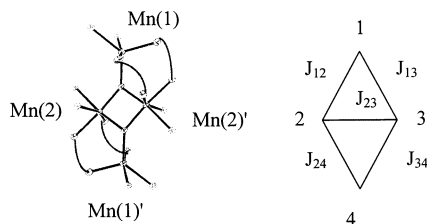


Fig. 3. The coupling scheme used to obtain a theoretical expression of χ_m vs. T for **1**.

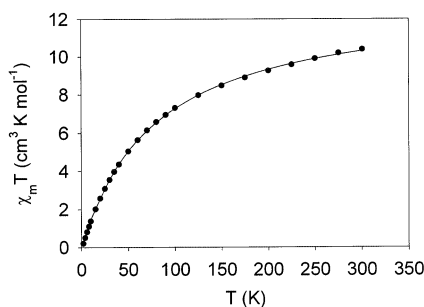


Fig. 4. $\chi_m T$ vs. T plot for **1**. The solid line represents the best fit described in the text.

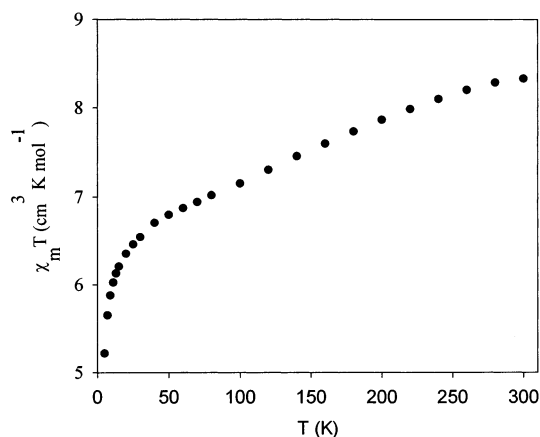


Fig. 5. $\chi_m T$ vs. T plot for **2**.

assigned as Mn(1), and the Mn(III) centers as Mn(2), Mn(3) and Mn(4). As in **1**, two dinuclear units are held together by two triply bridging oxides. Each Mn₂ unit is quadruply bridged by an oxide (O(5) and O(6)), a *syn*, *syn*-PhCO₂⁻ group, the ligand L and a methoxide group. Again, the bipyridine rings are essentially parallel, providing additional intramolecular and intermolecular interactions by π stacking.

3.2. Dc magnetic susceptibility

Variable temperature magnetic susceptibility data were collected on powdered polycrystalline samples of **1** and **2** restrained in eicosane to prevent torquing (SQUID magnetometer, 1 T). The data for **1** were fit to

a model (Fig. 3) that employed $-2JS_iS_j$ terms for the exchange interactions. In order to apply the Kambe vector coupling method, the approximation that $J_{12} = J_{12'} = J_{1'2'} = J_{1'2} = J_2$ was applied and a theoretical expression of χ_m versus T was derived; this approximation is reasonable because Mn(II)–Mn(III) interactions are all similarly very weak regardless of the Mn–O–Mn angle [6].

Complex **1** exhibits a $\chi_m T$ per molecule that smoothly decreases from 10.38 cm³ K mol⁻¹ at 300 K to 0.20 cm³ K mol⁻¹ at 2 K (Fig. 4), and the best fit gives $J_1 = -4.3$ cm⁻¹, $J_2 = -3.9$ cm⁻¹ and $g = 1.8$. The value of J_2 shows that significant interfragment interactions exist in **1**. The variable-field and variable-temperature data in the 2–30 K temperature range and 1–7 T magnetic field range indicate that **1** has a $S = 1$ spin ground state.

Complex **2** exhibits a $\chi_m T$ per molecule that gradually decreases from 8.32 cm³ K mol⁻¹ at 300 K to 6.79 cm³ K mol⁻¹ at 50 K, and then sharply decreases to 5.21 cm³ K mol⁻¹ at 5 K (Fig. 5). The sharp decrease observed at low temperatures is most likely due to intermolecular interactions, such as the π stacking of the bipyridine rings observed in the crystal structure. The $\chi_m T$ value at 300 K is less than the spin-only value for one Mn(II) and three Mn(III) that are non-interacting (14.17 cm³ K mol⁻¹) indicating the presence of antiferromagnetic interactions between the metals. Five exchange parameters are required in order to describe the pairwise interactions in **2** and a simple approach such as the one used for **1** cannot be applied in this case. Reduced magnetization measurements in the 2–30 K temperature range and 1–5 T magnetic field range can be fitted for a $S = 7/2$ spin ground state, $g = 1.8$ and $D = -0.7$ cm⁻¹.

Our previous experience shows that both global and local minima can be encountered in fits of data for [Mn₄O₂] and an error surface calculation was considered to address the reliability regarding the ground state of **1**. The error surface was generated as a function of J_1 and J_2 , with $g = 1.8$ for **1**. The absolute minimum lies in the spin ground state predicted by the reduced magnetization plots and the theoretical model, i.e. $|S, S_{23}, S_{14}\rangle$ are $|1, 4, 5\rangle$ for **1**. The observed spin ground states for **1** and **2** can be explained by the presence of spin frustration, defining the latter in the sense of the presence of competing exchange interactions of comparable magnitude that prevent (frustrate) the preferred spin alignments [6]. In both cases, antiferromagnetic coupling is observed, but it is clearly impossible for the spins of each Mn center to be aligned antiparallel to each of the three neighbouring spins. Such a situation leads to the ground state becoming particularly sensitive to the relative magnitude of the competing interactions (i.e. the J_1/J_2 ratio), and the spin of the ground state adopts an intermediate value ($S = 1$

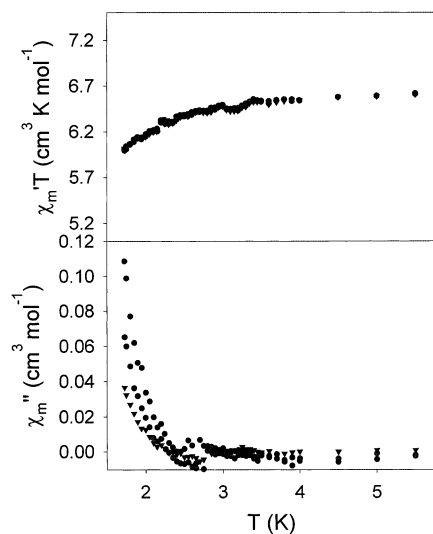


Fig. 6. In-phase and out-of-phase ac magnetic susceptibility vs. temperature plots for **2**.

for **1** and $S = 7/2$ for **2**) rather than the lowest value ($S = 0$) that might be predicted for a completely antiferromagnetically coupled system.

3.3. Ac magnetic susceptibility

Evidence for complex **2** functioning as a SMM was obtained with Ac magnetic susceptibility measurements. If, as indicated by the reduced magnetization plot, the complex possesses zero field splitting and the D value is negative (as usually observed for Mn(III) complexes), then the $S = 7/2$ ground state would be split into $m_s = \pm 7/2, \pm 5/2, \pm 3/2$ and $\pm 1/2$ levels. Negative ZFS and a large spin ground state are required for a molecule to function as a SMM. The magnetic moment of a SMM can be magnetized with its spin either up or down along the magnetic anisotropy axis; if the magnetic field is removed, the moment of the molecule will reorient very slowly if the temperature is low enough. A frequency dependent out-of-phase ac magnetic susceptibility (χ''_m) signal is a good indicator that a molecule is a SMM. A powdered polycrystalline sample of **2** was studied in the 1.7–12 K range with a 3.5 G ac field oscillating at 500, 1000 and 1500 Hz (Fig. 6). At temperatures below 3 K there are signs of slow relaxation for complex **2**, although no peak maximum is observed above 1.7 K. The value of $\chi'_m T$ decreases from $6.45 \text{ cm}^3 \text{ K mol}^{-1}$ at 3.0 K to $6.00 \text{ cm}^3 \text{ K mol}^{-1}$ at 1.7 K. This is accompanied by the appearance of a frequency dependent χ''_m signal at the same temperatures.

This identifies complex **2** as a new addition to the SMM family.

4. Conclusion

A new structural type in Mn_4 chemistry, complex **2**, has been synthesized and fully characterized. The magnetic properties of **1** and **2** have been studied, both complexes displaying antiferromagnetic coupling. The spin ground states of **1** and **2** have been determined and can be rationalized using the concept of spin frustration. Complex **2** has been identified as a new addition to the SMM family. Magnetization hysteresis and low temperature studies are in progress.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 151748. Copies of this information may be obtained from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1233-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

Acknowledgements

This work has been supported by NIH grant GM 39083.

References

- [1] (a) S.M.J. Aubin, M.W. Wemple, D.M. Adams, H.L. Tsai, G. Christou, D.N. Hendrickson, *J. Am. Chem. Soc.* 119 (1996) 7746. (b) H.J. Eppley, H.L. Tsai, N. de Vries, K. Folting, G. Christou, D.N. Hendrickson, *J. Am. Chem. Soc.* 117 (1995) 301.
- [2] M.P. Klein, V.K. Yachandra, K. Sauer, *Chem. Rev.* 96 (1996) 2927.
- [3] T. Garber, S. Van Wallendael, D.P. Rillema, K. Martin, W.E. Hatfield, J.H. Welch, P. Singh, *Inorg. Chem.* 29 (1990) 2863.
- [4] (a) V.A. Grillo, S. Ziming, K. Folting, D.N. Hendrickson, G. Christou, *Chem. Commun.* (1996) 2233. (b) C.M. Grant, M.J. Knapp, W.E. Streib, J.C. Huffman, D.N. Hendrickson, G. Christou, *Inorg. Chem.* 37 (1998) 6065. (c) V.A. Grillo, M.J. Knapp, J.C. Bollinger, D.N. Hendrickson, G. Christou, *Angew. Chem. Int., Ed. Engl.* 35 (1996) 1818.
- [5] E.C. Sañudo, V.A. Grillo, J. Yoo, J.C. Huffman, J.C. Bollinger, D.N. Hendrickson, G. Christou, in preparation.
- [6] M.W. Wemple, S. Wang, H.L. Tsai, J.P. Claude, W.E. Streib, J.C. Huffman, G. Christou, D.N. Hendrickson, *Inorg. Chem.* 35 (1996) 6437.