

## MIXED VALENCE MANGANESE CARBOXYLATES OF VARIOUS NUCLEARITIES

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**ABSTRACT.** Synthetic procedures have been developed which yield mixed valence manganese compounds. The structures of these species are described. The products all involve discrete molecular species consisting, with one exception, of an oxide-bridged  $Mn_x$  core with peripheral ligation by a combination of carboxylates, neutral donor groups and/or  $Cl^-$  ions. In every case, trapped valency is observed. The intramolecular exchange interactions have been investigated by variable-temperature magnetic susceptibility studies, and both antiferromagnetic and ferromagnetic interactions have been observed. The obtained values of the exchange parameters  $J$  are tabulated.

### 1. Introduction

As part of a program directed towards the preparation of synthetic models for the various manganese biomolecules being identified, we have been seeking to develop methodology capable of yielding higher oxidation state ( $\geq II$ ) manganese aggregates. For biological modelling reasons, we have concentrated primarily on carboxylate ( $RCO_2^-$ ) ligands, although phenoxide-based ligands and neutral donor groups have also been employed.

The various synthetic procedures that have now been developed have yielded a large and growing family of Mn aggregates of various nuclearities (2-12). Some of these species have been found to be mixed-valence, and their structures are described, as are the results obtained by variable-temperature magnetic susceptibility studies.

### 2. Results

#### 2.1 SYNTHESSES AND STRUCTURES

The six complexes described in this work are listed below, together with their oxidation states. The procedures employed for their preparation have been described in detail elsewhere [1]. They all involve, as the starting point, the trinuclear  $Mn_3O(O_2CR)_6L_3^z$  ( $z = 0$  or

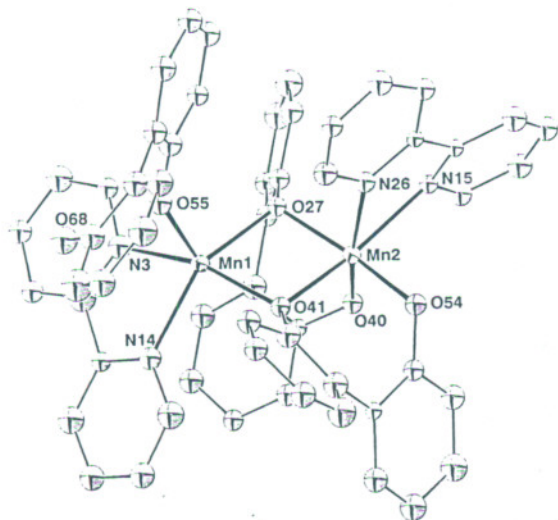


Figure 1. The structure of  $\text{Mn}_2(\text{biphen})_2(\text{biphenH})(\text{bpy})_2$  (**1**); the  $\text{Mn}^{\text{II}}$  and  $\text{Mn}^{\text{III}}$  sites are atoms Mn1 and Mn2, respectively.

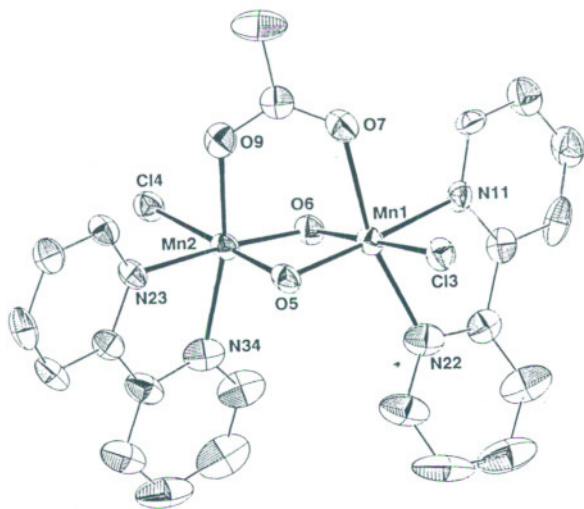


Figure 2. The structure of  $\text{Mn}_2\text{O}_2(\text{OAc})\text{Cl}_2(\text{bpy})_2$  (**2**); the  $\text{Mn}^{\text{III}}$  and  $\text{Mn}^{\text{IV}}$  sites are atoms Mn(2) and Mn(1), respectively.

<u>1</u>	$\text{Mn}_2(\text{biphen})_2(\text{biphenH})(\text{bpy})_2$	$\text{Mn}^{\text{II}}, \text{Mn}^{\text{III}}$
<u>2</u>	$\text{Mn}_2\text{O}_2(\text{OAc})\text{Cl}_2(\text{bpy})_2$	$\text{Mn}^{\text{III}}, \text{Mn}^{\text{IV}}$
<u>3</u>	$\text{Mn}_3\text{O}(\text{O}_2\text{CPh})_6(\text{py})_2(\text{H}_2\text{O})$	$\text{Mn}^{\text{II}}, 2\text{Mn}^{\text{III}}$
<u>4</u>	$(\text{ImH})_3[\text{Mn}_4\text{O}_3\text{Cl}(\text{OAc})_3]$	$3\text{Mn}^{\text{III}}, \text{Mn}^{\text{IV}}$
<u>5</u>	$\text{Mn}_6\text{O}_2(\text{O}_2\text{CPh})_{10}(\text{py})_2(\text{MeCN})_2$	$4\text{Mn}^{\text{II}}, 2\text{Mn}^{\text{III}}$
<u>6</u>	$\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CPh})_{16}(\text{H}_2\text{O})_4$	$8\text{Mn}^{\text{III}}, 4\text{Mn}^{\text{IV}}$

+) complexes, the latter being readily available in large amounts from  $\text{NBu}_4\text{MnO}_4$  [1]. The complexes are obtained as black crystals in good yield and high purity, and their structures have been elucidated by single-crystal X-ray techniques.

The structures of the complexes are displayed in Figures 1-6. It is clearly evident from examination of structural parameters that the complexes are trapped-valence and the figure captions therefore indicate the position of the various oxidation state Mn centres. All  $\text{Mn}^{\text{III}}$  sites show clear evidence of axial Jahn-Teller elongation as expected for high-spin  $d^4$  configurations. With the exception of 1, the complexes contain an  $[\text{Mn}_x\text{O}_y]$  core involving either  $\mu_2$ - or  $\mu_3$ -oxide ions; peripheral ligation is then primarily by carboxylates. Complex 1 is different in the sense that the metals are bridged by phenoxide oxygen atoms, and there are no carboxylate groups.

## 2.2 MAGNETIC EXCHANGE INTERACTIONS

Magnetochemical studies have been performed on complexes 1-6 in collaboration with D. N. Hendrickson and co-workers at the University of California at San Diego. Variable-temperature solid-state magnetic susceptibility measurements were made in the temperature range 5-300K, and the data were least-squares fit to the appropriate theoretically-derived  $\chi_m$  vs T expression for complexes 1-5. For complex 6, the appropriate theoretical expression has yet to be derived. The obtained values of the exchange parameter J are listed in Table I, together with the resulting spin ground states.

TABLE I. Exchange Interactions<sup>a</sup> and Spin Groundstates

Complex	J/cm <sup>-1</sup>	S
<u>1</u> $\text{Mn}_2(\text{biphen})_2(\text{biphenH})(\text{bpy})_2$	+0.86 (II/III)	9/2
<u>2</u> $\text{Mn}_2\text{O}_2(\text{OAc})\text{Cl}_2(\text{bpy})_2$	-114.0 (III/IV)	1/2
<u>3</u> $\text{Mn}_3\text{O}(\text{O}_2\text{CPh})_6(\text{py})_2(\text{H}_2\text{O})$	-7.3 (II/III)	1/2
	-10.9 (III/III)	
<u>4</u> $\text{Mn}_4\text{O}_3\text{Cl}_7(\text{OAc})_3^{3-}$	+12.1 (III/III)	9/2
	-16.0 (III/IV)	
<u>5</u> $\text{Mn}_6\text{O}_2(\text{O}_2\text{CPh})_{10}(\text{py})_2(\text{MeCN})_2$	-2.4 (II/II)	0
	-0.8 (II/III)	
	-42.0 (III/III)	
<u>6</u> $\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CPh})_{16}(\text{H}_2\text{O})_4$	---	14

<sup>a</sup> based on the  $H = -2JS_i \cdot S_j$  convention

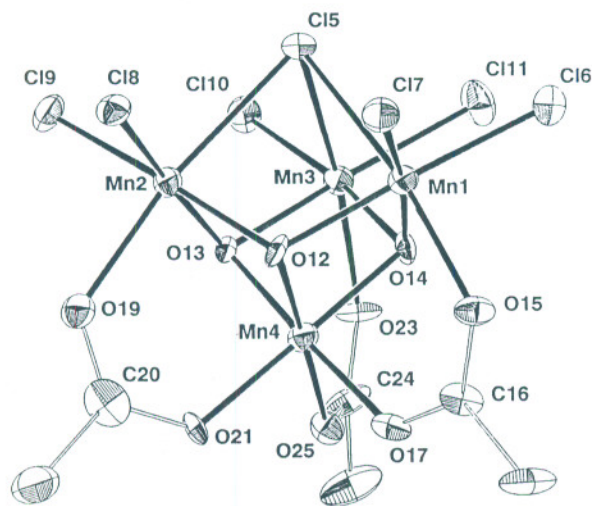


Figure 3. The structure of  $\text{Mn}_3\text{O}(\text{O}_2\text{CPh})_6(\text{py})_2(\text{H}_2\text{O})$  (**3**); the  $\text{Mn}^{\text{II}}$  site is atom Mn(3), and the  $\text{H}_2\text{O}$  oxygen atom is O(5).

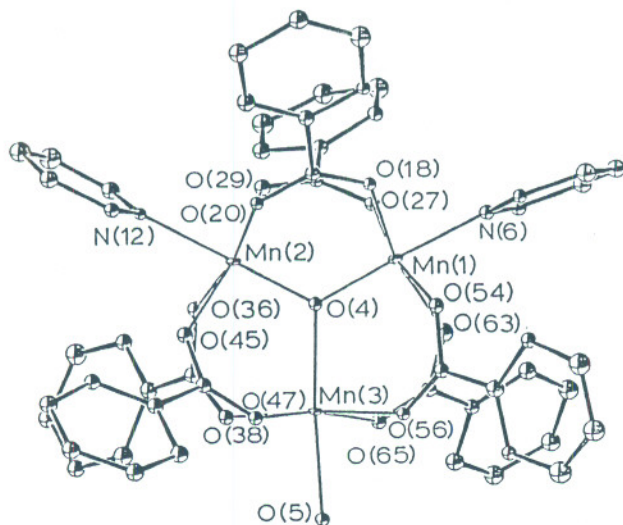


Figure 4. The structure of the anion of  $(\text{ImH})_3[\text{Mn}_4\text{O}_3\text{Cl}_7(\text{OAc})_3]$  (**4**); the  $\text{Mn}^{\text{IV}}$  site is atom Mn4.



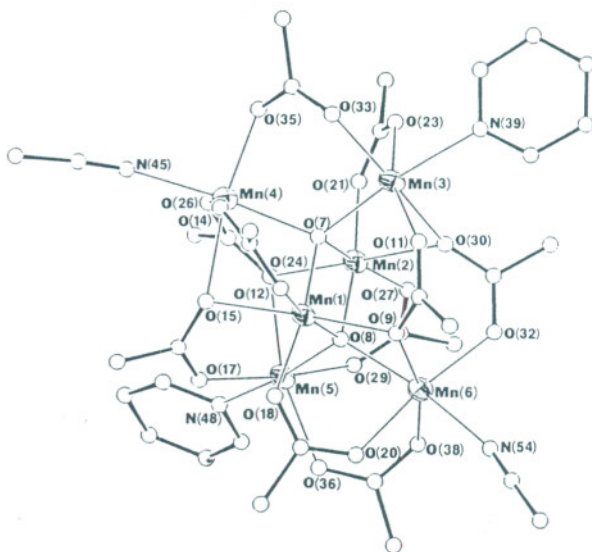


Figure 5. The structure of  $\text{Mn}_6\text{O}_2(\text{O}_2\text{CPh})_{10}(\text{py})_2(\text{MeCN})_2$  (**5**) showing only one phenyl carbon atom to avoid congestion; the  $\text{Mn}^{\text{IV}}$  sites are Mn(1) and Mn(2).

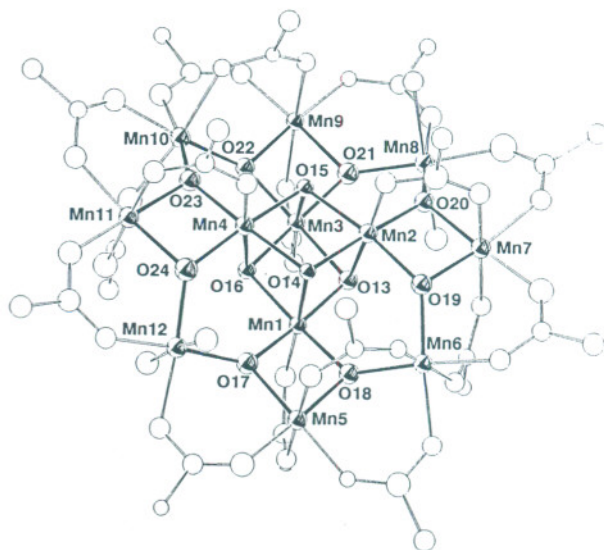


Figure 6. The structure of  $\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CPh})_{16}(\text{H}_2\text{O})_4$  showing only one phenyl carbon atom to avoid congestion; the  $\text{Mn}^{\text{IV}}$  sites are atoms Mn1-Mn4, and the  $\text{H}_2\text{O}$  groups are bound to atoms Mn8 and Mn12.

It is evident from the table that the exchange interactions are relatively weak ( $|J| = 0.8-114.0 \text{ cm}^{-1}$ ) and that both positive (ferromagnetic) and negative (antiferromagnetic)  $J$  values have been observed. This has resulted in complexes 1 and 4 having  $S = 9/2$  ground states. Complex 6 was investigated by magnetization vs field strength studies to probe the ground state, and it has been discovered that it possesses a remarkable  $S = 14$  ground state, the highest yet observed for a discrete molecule.

### 3. Conclusions

A variety of mixed-valence manganese complexes can be readily prepared. They encompass a wide range of nuclearities and are trapped-valence, presumably as a result of the structural deformations of the Jahn-Teller effect. These species have interesting and varied structures, and possess unusual magnetic properties.

### 4. Acknowledgments

The work described was supported by the U.S. National Science Foundation and National Institutes of Health.

### Reference

- [1] Christou, G. (1989) 'Manganese carboxylate chemistry and its biological relevance', *Acc. Chem. Res.* 22, 328-335.