

# Synthesis and Magnetic Properties of a $\mu$ -Oxo-di( $\mu$ -acetato)-manganese(III) Complex of a Strapped Tripodal Pyridylamine Ligand $N,N,N',N'$ -Tetrakis(2-pyridylmethyl)-1,3-propanediamine. A Model for the $Mn_2$ Site of Mn-Catalase Enzymes

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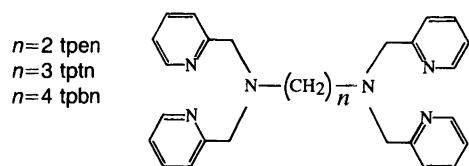
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A  $\mu$ -oxo-di( $\mu$ -acetato)-bridged manganese(III) complex  $[Mn_2O(CH_3CO_2)_2tptn](ClO_4)_2 \cdot CH_3CN$  (**1**) has been synthesized from reaction of basic  $Mn^{III}$  acetate and the 'strapped' tripodal ligand  $N,N,N',N'$ -tetrakis(2-pyridylmethyl)-1,3-propanediamine, tptn. The magnetic and electronic spectral data of **1** are generally similar to those of structurally characterized triazacyclononane and tris-(1-pyrazolyl)borate analogues and to those of manganese-catalase enzymes indicating a common core metallo-structure in all cases. Variable-temperature magnetic data on **1** are indicative of ferromagnetic coupling between  $Mn^{III}$  ions ( $J = +11 \text{ cm}^{-1}$ ), a phenomenon recently observed in other related polynuclear  $Mn^{III}$  species.

There is intense activity in a number of laboratories in trying to synthesize good model compounds of manganese in order to mimic aspects of the active sites of the photosynthetic water oxidation centre (WOC in Photosystem II) and of certain Mn-enzymes.<sup>1–4</sup> While the metal-site structures of these biomolecules are still not particularly well understood it is thought that the catalases (e.g. *Lactobacillus plantarum*<sup>5</sup>) probably contain  $\mu$ -oxo-di( $\mu$ -carboxylato) $Mn_2$  dinuclear moieties and the WOC probably contains dinuclear or tetranuclear oxo/hydroxy bridged species bonded to the protein via N- or O-donor groups.<sup>6</sup> ESR-active states of both classes of protein, which give rise to multiline signals, are generally thought to involve mixed-valence  $Mn^{III/IV}$  or  $Mn^{III/III}$  neighbours. Changes in magnetic susceptibility between the WOC oxidation states have recently been reported and related to existing model systems.<sup>7</sup>

Our own approaches to modelling  $\mu$ -oxo/hydroxo polynuclear manganese species involve the use of a number of types of dinucleating ligands. In the present study we report the use of a strapped tripodal pyridylamine ligand, tptn, (shown) which we have previously used to obtain a good model for the iron protein, hemerythrin.<sup>8</sup>



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This ligand forms an  $Mn^{III}$  compound of formula  $[Mn_2O(CH_3CO_2)_2tptn](ClO_4)_2$  (**1**), the spectral and magnetic properties of which, described here, are similar to those displayed by the Mn-catalase enzymes referred to above.

## Experimental

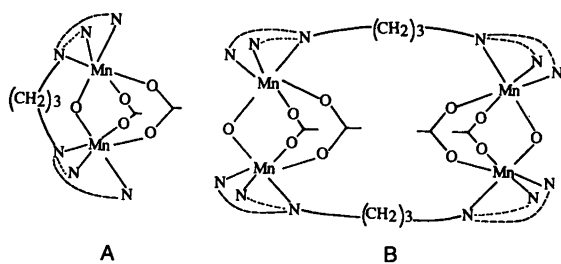
The ligand tptn was synthesised using a literature method.<sup>9</sup> Magnetic and spectral measurements were made using equipment described previously.<sup>10</sup> An applied field of 10 kOe was used for the susceptibility measurements and neat, powdered samples of **1** were employed.

*Synthesis of  $[Mn_2O(CH_3CO_2)_2tptn](ClO_4)_2 \cdot CH_3CN$  (**1**).*  $N,N,N',N'$ -Tetrakis(2-pyridylmethyl)-1,3-propanediamine (tptn) (660 mg, 1.5 mmol) and sodium perchlorate (500 mg) were dissolved in acetonitrile (40 ml). The solution was heated to 45 °C and basic manganese(III) acetate (530 mg, 1.0 mmol) was added with stirring. The mixture was filtered after 15 min and the filtrate was transferred to a glass cylinder. A layer of hexane (30 ml) was carefully placed on top of the brown solution. The glass was closed tightly and the mixture was left undisturbed at room temperature for 10 days. During this time large red-brown crystals were precipitated. They were removed by filtration and washed with a 1:1 mixture of tetrahydrofuran and hexane. Yield 0.27 g (19.5%). Anal.  $C_{33}H_{39}Cl_2Mn_2N_7O_{13}$ : C, H, N. These crystals rapidly lost  $CH_3CN$  in air. More stable crystals were obtained on recrystallisation from  $H_2O-CH_3CN$ , and these were employed in X-ray crystallographic attempts.

Microanalysis indicated that these contained no  $\text{CH}_3\text{CN}$ , but rather  $2\text{H}_2\text{O}$ .

## Results and discussion

Complex **1** was obtained in the form of large red-brown crystals by reacting manganese(III) acetate, tptn and sodium perchlorate together in acetonitrile as solvent. Water-containing solutions can not be used for synthesis, since disproportionation of the  $\text{Mn}^{\text{III}}\cdots\text{Mn}^{\text{III}}$  species occurs. Once formed, the complex can be recrystallised from aqueous MeCN solutions. Crystals obtained this way unfortunately do not diffract X-rays well because of their layered habit. Changing the anion from  $\text{ClO}_4^-$  to  $\text{PF}_6^-$  did not improve matters. The stoichiometry, oxidation state and core structure ( $\mu$ -oxo-di- $\mu$ -acetato) of **1** is undoubtedly correct as judged by analytical data, and by the close agreement of IR and electronic spectral data of **1** with those of a related triazacyclononane compound (**2**) recently reported by Wiegardt *et al.*<sup>1</sup> and with those of the structurally characterised complex  $[\text{Fe}_2\text{O}(\text{CH}_3\text{CO}_2)_2\text{tpbn}]_2(\text{ClO}_4)_4$ .<sup>8</sup> Since a powder diffractogram of **1** is not the same as that of the  $\text{Fe}^{\text{III}}$ -tptn analogue and since the magnetic data (*vide infra*) can be fitted extremely well to a dinuclear model, it is possible that the molecular structure of **1** is dinuclear as in (A) rather than tetranuclear as was initially anticipated; viz. (B).<sup>8</sup> However, while it is known from related work<sup>11,12</sup> dealing with 'strapped' complexes of  $\text{Cu}_2(\text{OMe})_2$  cores that a trimethylene group is capable of spanning a Cu-Cu distance of 3.07 Å, and it is known that the Mn $\cdots$ Mn distances in three reported  $\text{Mn}(\mu\text{-O})(\mu\text{-CH}_3\text{CO}_2)_2\text{Mn}$  cores lie in the range 3.08–3.15 Å,<sup>1,2,13</sup> the adoption of structure A is not



very likely in view of the steric strain which would occur if the  $(\text{CH}_2)_3$  strap and the  $\mu$ -oxo O atom were in the same plane.\*

The magnetic and electronic spectral data on **1** are given in Table 1 and compared with those of the recently reported triazacyclononane<sup>1</sup> and hydrotris-(1-pyrazolyl)borate<sup>2</sup> analogues **2** and **3**. The visible spectra of all three compounds are similar to each other and to those reported for the manganese catalase of *Lactobacillus plantarum*<sup>14</sup> and for a ribonucleotide reductase of *Brevibacterium ammonia-*

\* Note added in proof: Structure B has recently been confirmed elsewhere by X-ray crystallographic studies.<sup>29</sup>

Table 1. Properties of complex **1** and of related  $\mu$ -oxo-di- $\mu$ -acetatomanganese(III) complexes.

Complex	<b>1</b>	<b>2</b> <sup>a</sup>	<b>3</b> <sup>b</sup>
UV-VIS			
( $\text{CH}_3\text{CN}$ , 20°C), $\lambda_{\text{max}}/\text{nm}$	202( $1.9 \times 10^4$ )	232( $3.4 \times 10^3$ )	283( $1.2 \times 10^4$ )
( $\epsilon$ per $\text{Mn}_2/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ )	257( $1.0 \times 10^4$ ) 370sh( $1.2 \times 10^3$ )	280( $3.8 \times 10^3$ ) 560sh	385sh(910) 458sh(330) 486(420) 503sh(380) 524sh(350) 540sh(330)
	494(191)	495(324)	572sh(50) 680(10) 820(20)
	531(100) 550sh(73)	520(250) 545sh 560sh	582sh(190) 760(116)
Magnetism	ferromagnetic	ferromagnetic <sup>c</sup>	weakly anti-ferromagnetic
	$g=1.95$ $J=11 \text{ cm}^{-1}$ $D^d=7 \text{ cm}^{-1}$	$g=2.0$ $J=9 \text{ cm}^{-1}$ $D=3 \text{ cm}^{-1}$	$J \approx -0.2$ to $-0.7 \text{ cm}^{-1}$

<sup>a</sup>Complex **2** is  $[(\text{tacn})_2\text{Mn}^{\text{III}}(\mu\text{-O})(\mu\text{-CH}_3\text{CO}_2)_2](\text{ClO}_4)_2$ , where tacn = 1,4,7-triazacyclononane. <sup>b</sup>Complex **3** is  $[(\text{HB}(\text{pz})_3)_2\text{Mn}_2^{\text{III}}(\mu\text{-O})(\mu\text{-CH}_3\text{CO}_2)_2]$  where  $\text{HB}(\text{pz})_3$  is hydrotris(1-pyrazolyl)borate. <sup>c</sup>The magnetic data are actually for the trimethyl-*N*-substituted tacn complex (Ref. 1). <sup>d</sup>The  $D$  term allows for single-ion zero-field splitting.

genes,<sup>15</sup> indicating a probable common core metallostructure in all cases.

The temperature variation of the magnetic moment, per manganese atom, is shown in Fig. 1.  $\mu_{\text{Mn}}$  increases from 5.22 B.M. towards a plateau value of  $\sim 6.05$  B.M. as the temperature decreases from 300 to 30 K. It then decreases rapidly to a value of 5.07 B.M. at 4.3 K. The 300–30 K region is typical of the behaviour expected for ferromagnet-

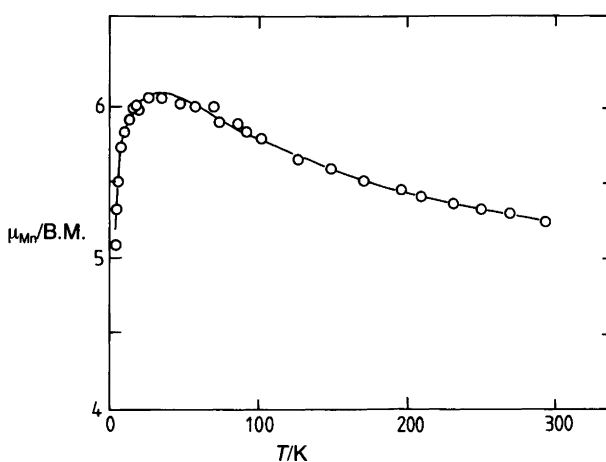


Fig. 1. Temperature dependence of magnetic moment, per Mn atom of complex **1** using a 10 kOe applied field. The calculated line uses the  $g$ ,  $J$  and  $D$  values given in Table 1. See text for comments on other fitting attempts.

ically coupled  $\text{Mn}^{\text{III}}\text{-Mn}^{\text{III}}$  ( $S=2/S=2$ ) pairs in which the ground state is a  $S'=4$  spin state. The rapid decrease in  $\mu_{\text{Mn}}$  at very low temperatures is similar to that observed in various ferromagnetically coupled  $\text{Ni}_2^{16}$  and  $\text{Cu}_2^{17}$  compounds and is due to single-ion zero-field splitting effects and/or to weak intermolecular antiferromagnetic coupling, both of which give rather similar low-temperature behaviour. Inclusion of a  $(T-\theta)$  term into the Van Vleck susceptibility expression for an  $S=2$  dimer gave a very good fit using  $J=10.2\text{ cm}^{-1}$  and  $\theta=-2\text{ K}$ , where the latter term allows for intermolecular antiferromagnetic effects.<sup>16</sup> A similarly good fit, shown in Fig. 1, is obtained using the thermodynamic expression for susceptibility together with a matrix diagonalization approach employing a spin Hamiltonian containing exchange ( $-2JS_1 \cdot S_2$ ) and axial zero-field splitting terms ( $D_1=D_2=D$ ).<sup>10</sup> The calculated line in Fig. 1 is for  $g=1.95$ ,  $J=11\text{ cm}^{-1}$  and  $D=7\text{ cm}^{-1}$ , the last parameter influencing the low-temperature decrease in  $\mu_{\text{Mn}}$ . Interestingly, it is also possible to fit this low-temperature region using  $D=-3\text{ cm}^{-1}$ . More precise refinement of the parameters would require variable field magnetization and single-crystal anisotropy measurements at low temperatures.<sup>10,18</sup>

Wieghardt *et al.*<sup>1</sup> have recently reported virtually identical magnetic behaviour for an *N*-methyl-substituted triaza-cyclononane complex of **2**, the only differences being a slightly higher  $\mu_{\text{max}}$  value (6.16 B.M. at 26 K) and  $\mu_{4.3\text{K}}$  value (ca. 5.9 B.M.) obtained in a 1 kOe applied field. These workers also employed a spin Hamiltonian approach containing  $J$  and  $D$  terms and obtained a value of  $J$  very similar to that for **1**. It is therefore likely that the core geometries in **1** and **2**, and perhaps the capping ligand geometries, are similar. Surprisingly, complex **3**, which contains the  $\text{HB}(\text{pz})_3^-$  capping ligand, shows<sup>2</sup> very weak antiferromagnetic behaviour, and this difference compared to **1** and **2** might be related to subtle differences observed in the core geometry. Similar arguments apply to  $[\text{Mn}_2\text{O}(\text{OAc})_2\text{bipy}_2(\text{H}_2\text{O})_2](\text{PF}_6)_2$ , for which  $J=-3.4\text{ cm}^{-1}$ ,<sup>13</sup> and  $[\text{Mn}_2\text{O}(\text{OAc})_2\text{bipy}_2(\text{N}_3)_2]$ , for which  $J=3.4\text{ cm}^{-1}$ .<sup>18</sup>

Intramolecular ferromagnetic coupling between  $\text{Mn}^{\text{III}}$  neighbours bridged by oxo and carboxylato groups has also recently been observed in other polynuclear/mixed-valence Mn complexes such as  $[\text{Mn}_4\text{O}_3\text{Cl}_4(\text{OAc})_3(\text{py})_3]$  ( $J=12.1\text{ cm}^{-1}$ )<sup>19</sup> and  $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CPh})_{16}(\text{H}_2\text{O})_4]$ .<sup>20</sup> The Jahn-Teller distorted  $t_{2g}^3e_g^1$   $\text{Mn}^{\text{III}}$  configuration, and its associated arrangement of 'magnetic' orbitals would appear to be particularly prone to creating superexchange pathways and orbital overlap which lead to net ferromagnetic coupling.

Finally, some observations on the EPR spectrum of **1** are briefly described. Dissolution in pure dry DMF and immediate freezing to 77 K yields a well resolved 16-line signal at high instrument gain. These lines are centred at  $g \approx 2.02$  with  $^{55}\text{Mn}$ -hyperfine splitting of ca. 80 G. The complete line-shape is similar to those reported for  $\mu$ -dioxo  $\text{Mn}^{\text{III}}\text{-Mn}^{\text{IV}}$  dimers<sup>2,21,22</sup> and for Mn-catalase.<sup>5</sup>

It is generally assumed that even-spin  $\text{Mn}^{\text{III}}$  monomers ( $S=2$ ) or  $\text{Mn}^{\text{III}}\text{-Mn}^{\text{III}}$  dimers ( $S'=4,3,2,1,0$ ) are EPR-silent,

particularly in the  $g \sim 2$  region, because of a combination of non-Kramers degeneracy, zero-field splitting and adverse relaxation rate effects. Conversely, the  $S'=1/2$  ground-state systems in exchange-coupled  $\text{Mn}^{\text{III}}\text{-Mn}^{\text{IV}}$  models<sup>21,22</sup> and in the  $S_2$  oxidation level of Photosystem II<sup>6</sup> would be expected to yield a multiline  $g=2$  signal, as would the uneven-spin ( $S'=1/2$ ) sub-levels in some recently reported ferromagnetically coupled mixed-valence models.<sup>19,23</sup> Even-spin pair level spectra have been detected, however, in  $\text{Fe}^{\text{III}}\text{-O-Fe}^{\text{III}}$  ( $S'=2$  level)<sup>24</sup> and  $\text{Mn}^{\text{II}}\text{-O-Mn}^{\text{II}}$  ( $S'=2$  and higher levels)<sup>25</sup> systems.

Observations of multiline spectra of the present type for complexes containing the  $\text{Mn}^{\text{III}}_2\text{O}(\text{OAc})_2$  core are controversial. Nishida *et al.*<sup>26</sup> have reported similar observations for frozen DMF glasses of complexes related to **1**, and of complex **2**. They assign the lines to a superposition of 11-line hyperfine multiplets arising from the  $\text{Mn}^{\text{III}}\text{-Mn}^{\text{III}}$  pair levels  $S'=2,3,4$ . Wieghardt *et al.*,<sup>27</sup> however, claim that glasses of **2** are EPR-silent and that Nishida's observations are artefacts caused by the easy disproportionation of the  $\text{Mn}^{\text{III}}\text{-Mn}^{\text{III}}$  complex to the mixed-valence  $\text{Mn}^{\text{III}}\text{-Mn}^{\text{IV}}$  analogue.<sup>1,2</sup>

At this point we favour Wieghardt's interpretation, since it is possible, despite the care we took in handling the solutions of **1** used for EPR measurements, that a small quantity of the  $\text{Mn}^{\text{III}}\text{Mn}^{\text{IV}}$  complex had formed on the surface of the crystals prior to dissolution, or that traces of oxygen and water may have been present in the DMF solvent. Nevertheless, further studies of the EPR spectra of mono- and binuclear  $\text{Mn}^{\text{III}}$  complexes are generally warranted to eliminate these uncertainties, since complexes unrelated to **1** are reported to yield multiline signals.<sup>28</sup>

*Note added in proof:* Recent X- and Q-band studies of even-spin ground-state  $\text{Fe}(\text{II})\text{-Fe}(\text{II})$  ( $S'=4$ ) models display ESR lines at low field arising from transitions with non-Kramers doublets of the  $S'=4$  manifold.<sup>30,31</sup> Similar low-field signals have also just been reported for complex **3**, in this case arising from the  $S'=2$  levels.<sup>32</sup>

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