

Ground Spin State Variation in Carboxylate-Bridged Tetranuclear $[\text{Fe}_2\text{Mn}_2\text{O}_2]^{8+}$ Cores and a Comparison with Their $[\text{Fe}_4\text{O}_2]^{8+}$ and $[\text{Mn}_4\text{O}_2]^{8+}$ Congeners

Phalguni Chaudhuri,^{*,[a]} Eva Rentschler,^[a] Frank Birkelbach,^[a] Carsten Krebs,^[a]
Eckhard Bill,^[a] Thomas Weyhermüller,^[a] and Ulrich Flörke^[b]

Keywords: Oxo ligands / Carboxylate ligands / Iron / Manganese / Magnetic properties / Tetranuclear complexes

Syntheses of ten new tetranuclear complexes containing the $[\text{M}_\text{A}(\mu_3\text{-O})_2\text{M}_\text{B}]^{8+}$ butterfly core [$\text{M}_\text{A} = \text{M}_\text{B} = \text{Fe}^{\text{III}}$ (**1** and **2**), $\text{M}_\text{A} = \text{M}_\text{B} = \text{Mn}^{\text{III}}$ (**3** and **4**) and $\text{M}_\text{A} = \text{Fe}^{\text{III}}$, $\text{M}_\text{B} = \text{Mn}^{\text{III}}$ (**5–10**)] using 1,4,7-trimethyl-1,4,7-triazacyclononane (L) as the capping ligand, salicylaldoximate dianion (salox^{2-}) and six different carboxylate anions as bridging ligands, are described. The crystal structures of $[\text{L}_2\text{Fe}_2(\mu_3\text{-O})_2(\text{salox})_2(\text{diphenylglycolate})_3\text{Fe}_2](\text{ClO}_4)$ (**1**), $[\text{L}_2\text{Mn}_2(\mu_3\text{-O})_2(\text{salox})_2(\text{diphenylglycolate})_3\text{Mn}_2](\text{ClO}_4)$ (**3**), $[\text{L}_2\text{Fe}_2(\mu_3\text{-O})_2(\text{salox})_2(\text{acetate})_3\text{Mn}_2](\text{ClO}_4)$ (**5**), $[\text{L}_2\text{Fe}_2(\mu_3\text{-O})_2(\text{salox})_2(\text{diphenylglycolate})_3\text{Mn}_2](\text{ClO}_4)$ (**6**), and $[\text{L}_2\text{Fe}_2(\mu_3\text{-O})_2(\text{salox})_2(\text{benzoate})_3\text{Mn}_2](\text{ClO}_4)$ (**8**) were determined by X-ray crystallography. The complexes are isostructural, with M^{III} ions disposed in a butterfly core where bridging between the M^{III} ions occurs via two μ_3 -oxo anions. In complexes **5**, **6** and **8** the “wing-tip” positions of the butterfly are occupied by the LFe^{3+} units, whereas the “body” metal ions are d^4 high-spin Mn^{III} ions. Complexes **1–10** have been characterised by variable-tem-

perature (2–290 K) magnetic susceptibility measurements (1 T) and by Mössbauer spectroscopy. A “2J” model has been applied to simulate the experimental μ_{eff} vs. T plots. Overall exchange interactions are antiferromagnetic in nature. Complexes with the Fe_4O_2 core (**1** and **2**) and the Mn_4O_2 core (**3** and **4**) possess an $S_t = 0$ and $S_t = 3$ ground state, respectively, regardless of the nature of the bridging carboxylate ligand. In contrast, changing the bridging carboxylates in the $[\text{Fe}_2\text{Mn}_2\text{O}_2]$ core from acetate (**5**) to diphenylglycolate (**6**), triphenyl acetate (**7**), benzoate (**8**), chloroacetate (**9**) and propionate (**10**), results in a variation of the ground state from $S_t = 1$ to $S_t = 3$, due to spin frustration of the “body” manganese centres. The spin-correlation diagram for the $\text{Fe}_2\text{Mn}_2\text{O}_2$ butterfly arrangement clearly demonstrates the ground state variation as a function of the ratio of two competing coupling interactions.

(© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2003)

Introduction

Tetranuclear, oxide-bridged metal carboxylate assemblies are relevant to several areas including bioinorganic modelling and magnetochemistry. In the field of iron chemistry, the pursuit of model complexes for the iron proteins has yielded several interesting tetranuclear complexes^[1–6] amongst other polynuclear iron complexes with unusual electronic structures.^[7] The knowledge that in PSII the site of water oxidation is a tetranuclear manganese aggregate^[8] in which four manganese atoms are essential for activity and appear to be in close proximity to one another, has augmented the search for tetranuclear manganese complexes. Thus, tetramanganese butterfly^[6,9–12] complexes with the $[\text{Mn}_4\text{O}_2]^{8+}$ core have emerged as the most intensely studied oxide-bridged carboxylate clusters. Comparatively fewer studies of the butterfly $[\text{Fe}_4\text{O}_2]^{8+}$ core have been

made, and there are relatively few studies of the analogous heterometallic butterfly complexes,^[13,14] despite the fact that such studies might be more informative in comparison to those of homometal complexes. New exchange pathways can be expected for heteronuclear complexes,^[15–18] where unusual sets of magnetic orbitals can be brought into close proximity.

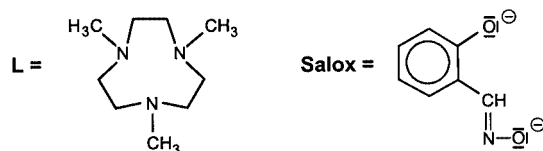
There are several intriguing features associated with oxo-bridged carboxylate clusters. Firstly, these complexes can have unusual electronic structures and may serve as sources of fundamental information about exchange coupling in multinuclear assemblies. A second general reason to study polynuclear metal complexes is that they may be building blocks for molecular-based magnetic materials.^[19] Because of their topology, molecules that have large numbers of unpaired electrons should serve as good starting points for constructing molecular magnetic materials. Even though the pairwise exchange interactions in these complexes are found almost always to be antiferromagnetic, spin frustration^[20,21] in the general sense of the term, or more accurately, competing spin interactions, can result in polynuclear complexes having a relatively large number of unpaired

^[a] Max-Planck-Institut für Strahlenchemie, Stiftstraße 34–36, 45470 Mülheim an der Ruhr, Germany
E-mail: Chaudh@mpi-muelheim.mpg.de

^[b] Anorganische und Analytische Chemie, Universität Paderborn, 33095 Paderborn, Germany

electrons in their ground states. Although spin frustration is a well-known magnetic phenomenon for extended lattices, its application to the magnetochemistry of discrete polynuclear complexes is not widely recognised. Competing spin interactions may give rise to unpredictable ground state spins and peculiar spin state spectra. Thus, the situation of ground state degeneracy induced by competing spin interactions is worth investigating.

We have been exploring the feasibility of using salicylaldehyde oxime to influence the nuclearity and metal topology of metal carboxylate complexes. Although salicylaldehyde oxime^[22] has been known as a metal-chelating agent since 1930, reports on the ligating properties of salicylaldehyde oxime towards trivalent transition metal ions are rare.^[23,24] Our approach of using oximes as ligands has yielded several interesting 3d metal complexes with the cores $[M_A(\text{oxime})_3M_B]^{n+}$,^[24] $[M_3^{\text{III}}(\mu_3\text{-O})(\mu_2\text{-OPh})]^{6+}$ ($M = \text{Ti, V, Cr, Mn, Fe and Co}$),^[25,26] $[M_6^{\text{III}}(\mu_3\text{-O})_2(\mu_2\text{-OOCR})_2]^{12+}$ ($M = \text{V, Cr, Mn, Fe}$)^[27] and $[(M_A^{\text{III}})_2(\mu_3\text{-O})_2(M_B^{\text{III}})_2]^{8+}$ ($M_A = M_B = \text{Fe}^{\text{III}},^{[4]} M_A = \text{Cr}^{\text{III}}, M_B = \text{Fe}^{\text{III}},^{[13]} M_A = \text{Cr}^{\text{III}}, M_B = \text{Mn}^{\text{III}}.$ ^[14] In this paper we report the extension of our studies to complexes having tetranuclear cores, and include the preparation and characterisation of $[\text{L}_2\text{Fe}_4(\mu_3\text{-O})_2(\mu_2\text{-OOCCH}(\text{OH})\text{Ph}_2)_3(\text{salox})_2]\text{ClO}_4$ (**1**), $[\text{L}_2\text{Fe}_4(\mu_3\text{-O})_2(\mu_2\text{-OOCCHPh}_3)_3(\text{salox})_2]\text{ClO}_4$ (**2**), $[\text{L}_2\text{Mn}_4(\mu_3\text{-O})_2(\mu_2\text{-OOCCH}(\text{OH})\text{Ph}_2)_3(\text{salox})_2]\text{ClO}_4$ (**3**), $[\text{L}_2\text{Mn}_4(\mu_3\text{-O})_2(\mu_2\text{-OOCCHPh}_3)_3(\text{salox})_2]\text{ClO}_4$ (**4**) and $[\text{L}_2\text{Fe}_2\text{Mn}_2(\mu_3\text{-O})_2(\mu_2\text{-carboxylate})_3(\text{salox})_2]\text{ClO}_4$ (**5–10**) [carboxylate = acetate (**5**), benzoate (diphenylglycolate) (**6**), triphenylacetate (**7**), benzoate (**8**), chloroacetate (**9**) and propionate (**10**)], where L is the cyclic amine 1,4,7-trimethyl-1,4,7-triazacyclononane and salox is the dianion of salicylaldehyde oxime (H_2salox). Molecules **1–10** contain M^{III} ions disposed in a butterfly $[\text{M}_4\text{O}_2]^{8+}$ core, where bridging between the M^{III} ions occurs via two $\mu_3\text{-oxo}$ anions.



Results

Our previous investigations of the use of solvolysis reactivity of $[\text{LFeCl}_3]^{[28]}$ in the synthesis of homo- and heteropolynuclear complexes led us to anticipate compounds with a butterfly structure, in which the “body” metal ions differ from the “wing-tip” (Fe^{3+}) ions. The fact that the iron centres remain bonded to the macrocyclic ligand L during the formation of the polynuclear complexes was recognised and subsequently utilised as a synthetic strategy for building $\text{Fe}_2(\text{O})_2\text{Mn}_2$ cores with Mn^{3+} as the “body” ions. Accordingly, the dark brown solution obtained from manganese(II) chloride, a carboxylic acid, salicylaldehyde oxime and triethylamine in methanol reacted with $[\text{LFeCl}_3]$ to afford, after addition of a perchlorate solution, dark brown crystals

of $[\text{L}_2\text{Fe}_2(\mu_3\text{-O})_2(\mu_2\text{-carboxylate})_3(\text{salox})_2\text{Mn}_2]\text{ClO}_4$ in reasonable yield. Complex **5** was prepared by using Mn^{III} acetate.

The IR spectra of the tetranuclear complexes **1–10** exhibit, besides ligand and ClO_4 absorptions, a sharp medium-intensity band in the region $670\text{--}660\text{ cm}^{-1}$, probably due to the ν_{asym} vibration of the four modes of the $\text{FeMn}_2(\mu_3\text{-O})$ triangle.^[29] The $\nu(\text{CN})$ vibration is assigned to the medium-intensity band at ca. 1600 cm^{-1} . One of the characteristics in the IR spectra is a strong carboxyl stretching vibration found in the region $1550\text{--}1580\text{ cm}^{-1}$. The complexes show a strong band, whose intensity is similar to that of $\nu(\text{COO})$, at ca. 1090 cm^{-1} (antisymmetric stretch) and a sharp band at ca. 620 cm^{-1} (antisymmetric bend), indicative of uncoordinated perchlorate anions.

Interestingly, the mass spectra of complexes **1–7** differ widely. Although the all-iron complexes **1** and **2** show signals due to the respective monocations $[M^+]$ with the expected isotope distributions in the ESI positive mode, the manganese compound **3** does not show the corresponding molecular ion. However, in the case of the mixed-metal complexes **5–7**, mass spectrometry in the ESI-positive mode has proved to be a very useful tool for characterisation.

Structures of Complexes 1 and 3

Figure 1 shows a perspective view of the cation of **1**. Although this complex contains an $[\text{Fe}_4(\mu\text{-diphenylglycolate})_3(\mu_3\text{-oxo})_2]$ core very similar to that in the previously reported $[\text{Fe}_4(\mu\text{-acetato})_3(\mu_3\text{-oxo})_2]$ complex,^[4] we have included the description of the structure of **1** in this paper to show that the OH groups of the diphenylglycolate ligands are not coordinated to the oxophilic Fe^{III} centres. It should also be noted that there are very few tetranuclear Fe^{III} complexes with the $[\text{Fe}_4\text{O}_2]^{8+}$ butterfly core reported

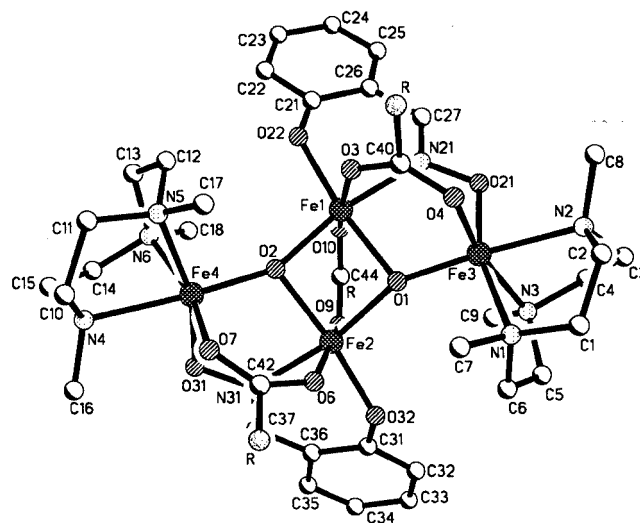


Figure 1. Structure of the monocation of complex **1**; the bridging diphenylglycolate (benzoate) anions are denoted by RCOO^- , i.e. “ $\text{Ph}_2\text{C}(\text{OH})$ ” has been replaced by “R” for clarity

Table 1. Selected bond lengths [Å] and angles [°] for 1

Fe(1)–O(22)	1.906(7)	Fe(1)–O(2)	1.949(7)
Fe(1)–O(1)	1.988(6)	Fe(1)–O(3)	2.109(6)
Fe(1)–O(10)	2.111(9)	Fe(1)–N(21)	2.115(10)
		Fe(2)–O(32)	1.910(8)
Fe(2)–O(1)	1.949(7)	Fe(2)–O(2)	1.981(7)
Fe(2)–N(31)	2.112(10)	Fe(2)–O(9)	2.130(6)
Fe(2)–O(6)	2.140(7)	Fe(3)–O(1)	1.874(7)
Fe(3)–O(21)	1.926(6)	Fe(3)–O(4)	2.031(10)
Fe(3)–N(3)	2.167(12)	Fe(3)–N(1)	2.204(11)
Fe(3)–N(2)	2.267(11)	Fe(4)–O(2)	1.872(7)
Fe(4)–O(31)	1.928(8)	Fe(4)–O(7)	2.039(8)
Fe(4)–N(6)	2.171(10)	Fe(4)–N(5)	2.217(10)
Fe(4)–N(4)	2.294(10)		
O(22)–Fe(1)–O(2)	104.2(3)	O(22)–Fe(1)–O(1)	172.6(3)
O(2)–Fe(1)–O(1)	83.0(3)	O(22)–Fe(1)–O(3)	87.4(3)
O(2)–Fe(1)–O(3)	96.8(3)	O(1)–Fe(1)–O(3)	90.3(3)
O(22)–Fe(1)–O(10)	84.8(3)	O(2)–Fe(1)–O(10)	94.7(3)
O(1)–Fe(1)–O(10)	96.2(3)	O(3)–Fe(1)–O(10)	167.4(3)
O(22)–Fe(1)–N(21)	85.3(4)	O(2)–Fe(1)–N(21)	169.5(3)
O(1)–Fe(1)–N(21)	87.6(3)	O(3)–Fe(1)–N(21)	88.1(4)
O(10)–Fe(1)–N(21)	81.4(4)	O(22)–Fe(1)–Fe(2)	144.0(3)
O(2)–Fe(1)–Fe(2)	44.1(2)	O(1)–Fe(1)–Fe(2)	43.3(2)
O(3)–Fe(1)–Fe(2)	109.7(2)	O(10)–Fe(1)–Fe(2)	82.2(2)
N(21)–Fe(1)–Fe(2)	125.4(3)	O(32)–Fe(2)–O(1)	104.0(3)
O(32)–Fe(2)–O(2)	172.8(3)	O(1)–Fe(2)–O(2)	33.2(3)
O(32)–Fe(2)–N(31)	86.3(4)	O(1)–Fe(2)–N(31)	166.5(3)
O(2)–Fe(2)–N(31)	86.5(3)	O(32)–Fe(2)–O(9)	83.9(4)
O(1)–Fe(2)–O(9)	92.3(3)	O(2)–Fe(2)–O(9)	95.3(3)
N(31)–Fe(2)–O(9)	79.9(4)	O(32)–Fe(2)–O(6)	88.0(3)
O(1)–Fe(2)–O(6)	99.8(3)	O(2)–Fe(2)–O(6)	91.3(3)
N(31)–Fe(2)–O(6)	89.1(3)	O(9)–Fe(2)–O(6)	166.8(3)
O(32)–Fe(2)–Fe(1)	143.1(2)	O(1)–Fe(2)–Fe(1)	44.4(2)
O(2)–Fe(2)–Fe(1)	43.2(2)	N(31)–Fe(2)–Fe(1)	122.7(2)
O(9)–Fe(2)–Fe(1)	80.0(2)	O(6)–Fe(2)–Fe(1)	112.4(2)
O(1)–Fe(3)–O(21)	96.4(3)	O(1)–Fe(3)–O(4)	97.4(3)
O(21)–Fe(3)–O(4)	92.4(4)	O(1)–Fe(3)–N(3)	96.8(4)
O(21)–Fe(3)–N(3)	92.7(4)	O(4)–Fe(3)–N(3)	164.3(4)
O(1)–Fe(3)–N(4)	100.5(4)	O(21)–Fe(3)–N(1)	162.6(4)
O(4)–Fe(3)–N(1)	89.6(5)	N(3)–Fe(3)–N(1)	81.2(5)
O(1)–Fe(3)–N(2)	176.0(4)	O(21)–Fe(3)–N(2)	85.5(4)
O(4)–Fe(3)–N(2)	86.1(5)	N(3)–Fe(3)–N(2)	79.6(5)
N(1)–Fe(3)–N(2)	77.5(4)	O(2)–Fe(4)–O(31)	95.7(3)
O(2)–Fe(4)–O(7)	98.2(3)	O(31)–Fe(4)–O(7)	91.8(3)
O(2)–Fe(4)–N(6)	96.4(3)	O(31)–Fe(4)–N(6)	95.3(4)
O(7)–Fe(4)–N(6)	163.0(4)	O(2)–Fe(4)–N(5)	100.5(3)
O(31)–Fe(4)–N(5)	163.7(4)	O(7)–Fe(4)–N(5)	87.5(4)
N(6)–Fe(4)–N(5)	81.3(4)	O(2)–Fe(4)–N(4)	176.2(3)
O(31)–Fe(4)–N(4)	86.3(4)	O(7)–Fe(4)–N(4)	85.0(4)
N(6)–Fe(4)–N(4)	80.1(4)	N(5)–Fe(4)–N(4)	77.4(4)
Fe(3)–O(1)–Fe(2)	155.8(4)	Fe(3)–O(1)–Fe(1)	111.7(3)
Fe(2)–O(1)–Fe(1)	92.4(3)	Fe(4)–O(2)–Fe(1)	155.5(4)
Fe(4)–O(2)–Fe(2)	111.8(3)	Fe(1)–O(2)–Fe(2)	92.6(3)
Fe(1)···Fe(2)	2.841(2)	Fe(2)···Fe(3)	3.738(2)
Fe(1)···Fe(3)	3.197(2)	Fe(2)···Fe(4)	3.192(2)
Fe(1)···Fe(4)	3.734(2)	Fe(3)···Fe(4)	6.077(2)

in the literature.^[1–6] The metal geometry of the cluster may be described as “butterfly” based on two edge-sharing Fe₃(μ₃-O) triangular units, with the oxygen atoms O(1) (0.029 Å) and O(2) (0.004 Å) above the corresponding Fe₃ triangles. The Fe(1)···Fe(2) distance [2.841(2) Å] is at the low end of the range (2.829–3.108 Å) observed in other [Fe₄O₂]-containing compounds.^[1–6] There are three types of independent Fe–O(oxo) distances, ranging from 1.872

to 1.988 Å, the two shortest being Fe(4)–O(2) [1.872(7) Å] and Fe(3)–O(1) [1.874(7) Å].

The dihedral angle between the planes Fe(1)Fe(2)Fe(3)O(1) and Fe(1)Fe(2)Fe(4)O(2) is 145.9°, which is slightly smaller than that in the corresponding acetate complex (153.9°). Selected bond lengths and angles for the Fe₄(μ₃-O)₂ core and for the rest of the cation are given in Table 1.

In addition to the two μ₃-oxo groups, there are three bridging carboxylate groups in the tetranuclear structure originating from the diphenylglycolate ion, one each between iron atom pairs Fe(4)Fe(2), Fe(1)Fe(2) and Fe(1)Fe(3). Additionally two N–O groups of the deprotonated salicylaldoximes are coordinated to iron atom pairs Fe(4)Fe(2) and Fe(3)Fe(1) through their oxygen and nitrogen donor atoms, respectively.

It should be noted that the enolic OH group of diphenylglycolic acid is not coordinated to any iron centre. It seems that the nonplanarity of the [Fe₄O₂]⁸⁺ unit is a consequence of the bridging carboxylate (diphenylglycolate) groups. Specifically, the carboxylate-bridged iron atoms are apparently “pulled” closer to one another [Fe(1)···Fe(3) = 3.197(2) Å, Fe(2)···Fe(4) = 3.192(2) Å] than those without carboxylate bridging [Fe(1)···Fe(4) = 3.734(2) Å, Fe(2)···Fe(3) = 3.738(2) Å]. Just as there are two long and two short Fe···Fe separations, there are also two long [Fe(1)–O(1) = 1.988(6) Å, Fe(2)–O(2) = 1.981(7) Å] and two short [Fe(2)–O(1) = 1.949(7) Å, Fe(1)–O(2) = 1.872(7) Å] iron–μ₃-oxo bonds in the inner Fe(1)Fe(2)O(1)O(2) core.

Each iron atom is in a distorted octahedral environment, with Fe(1) and Fe(2) having an FeNO₅ and Fe(3) and Fe(4) an FeN₃O₃ coordination sphere, respectively. Fe–N and Fe–O bond lengths are typical of high-spin ferric complexes. The Fe–N bonds *trans* to the short Fe–μ₃-O bonds are noticeably longer than those *cis* to them, as observed

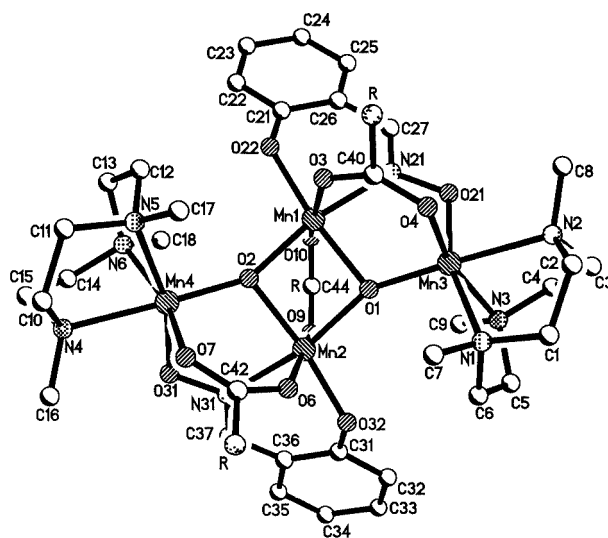


Figure 2. Perspective view of the cation of 3; “Ph₂C(OH)” -units of the bridging diphenylglycolate (benzilate) anions are denoted only by “R” for the sake of clarity

earlier.^[4] The structural parameters for **1** lie in the range reported for the other $[\text{Fe}_4\text{O}_2]^{8+}$ complexes.^[1–6]

A perspective view of the cation of complex **3** is shown in Figure 2, and selected structural parameters are listed in Table 2. The cation, like that in **1**, possesses an M_4O_2 core which can be considered as two edge-sharing Mn_3O units, the metal dispositions being a butterfly structure with Mn(1) and Mn(2) occupying the “body” sites and Mn(3) and Mn(4) occupying “wing-tip” sites. Each body-wing-tip and body-body Mn_2 pair is bridged by a carboxylate group of the diphenylglycolate anion in its common *syn,syn* binding mode. The μ_3 -O atoms O(1) and O(2) on each Mn_3 wing

of the butterfly are 0.04 and 0.008 Å, respectively, above their Mn_3 least-squares planes. The dihedral angle between the planes comprising Mn(1)Mn(2)Mn(3)O(1) and Mn(1)Mn(2)Mn(4)O(2) is 145.8°, a value identical with that in the Fe_4O_2 core of **1**. The shortest Mn...Mn contact is 2.844(2) Å, between Mn(1) and Mn(2). The coordination spheres of “wing-tip” [Mn(4) and Mn(3)], and “body” [Mn(1) and Mn(2)] manganese ions are MnN_3O_3 and MnNO_5 , respectively, in which the distortions along the axes O(3)Mn(1)O(10), O(6)Mn(2)O(9), N(2)Mn(3)O(1) and N(4)Mn(4)O(2) are as expected for Jahn–Teller-distorted high-spin d^4 ions in an octahedral geometry. The Mn–N and Mn–O bond lengths are consistent with a d^4 high-spin electronic configuration for the Mn^{III} centres. The essential features of the structure of the cation of **3** are very similar to those of **1**.

Table 2. Selected bond lengths [Å] and angles [°] for **3**

Mn(1)–O(22)	1.913(8)	Mn(2)–O(32)	1.904(8)
Mn(1)–O(2)	1.961(8)	Mn(2)–O(1)	1.959(8)
Mn(1)–O(1)	1.971(7)	Mn(2)–O(2)	1.966(8)
Mn(1)–O(10)	2.107(9)	Mn(2)–N(31)	2.101(10)
Mn(1)–N(21)	2.109(10)	Mn(2)–O(9)	2.116(9)
Mn(1)–O(3)	2.117(9)	Mn(2)–O(6)	2.125(9)
Mn(3)–O(1)	1.872(8)	Mn(4)–O(2)	1.869(8)
Mn(3)–O(21)	1.938(9)	Mn(4)–O(31)	1.926(8)
Mn(3)–O(4)	2.048(11)	Mn(4)–O(7)	2.048(9)
Mn(3)–N(3)	2.170(13)	Mn(4)–N(6)	2.167(11)
Mn(3)–N(1)	2.198(13)	Mn(4)–N(5)	2.221(11)
Mn(3)–N(2)	2.281(12)	Mn(4)–N(4)	2.267(11)
O(22)–Mn(1)–O(2)	103.9(3)	O(32)–Mn(2)–O(1)	104.5(4)
O(22)–Mn(1)–O(1)	173.0(3)	O(32)–Mn(2)–O(2)	172.4(4)
O(2)–Mn(1)–O(1)	82.9(3)	O(1)–Mn(2)–O(2)	83.1(3)
O(22)–Mn(1)–O(10)	85.1(4)	O(32)–Mn(2)–N(31)	86.0(4)
O(2)–Mn(1)–O(10)	94.8(3)	O(1)–Mn(2)–O(31)	166.0(4)
O(1)–Mn(1)–O(10)	96.5(4)	O(2)–Mn(2)–N(31)	86.5(4)
O(22)–Mn(1)–N(21)	86.1(4)	O(32)–Mn(2)–O(9)	83.8(4)
O(2)–Mn(1)–N(21)	169.1(4)	O(1)–Mn(2)–O(9)	91.6(4)
O(1)–Mn(1)–N(21)	87.4(4)	O(2)–Mn(2)–O(9)	95.5(4)
O(10)–Mn(1)–N(21)	81.5(4)	N(31)–Mn(2)–O(9)	80.2(4)
O(22)–Mn(1)–O(3)	86.4(3)	O(32)–Mn(2)–O(6)	87.6(4)
O(2)–Mn(1)–O(3)	96.8(3)	O(1)–Mn(2)–O(6)	100.6(3)
O(1)–Mn(1)–O(3)	90.9(3)	O(2)–Mn(2)–O(6)	91.6(3)
O(10)–Mn(1)–O(3)	166.9(3)	N(31)–Mn(2)–O(6)	88.9(4)
N(21)–Mn(1)–O(3)	88.1(4)	O(9)–Mn(2)–O(6)	166.5(4)
O(1)–Mn(3)–Mn(1)	34.8(2)	O(2)–Mn(4)–O(31)	95.4(4)
O(21)–Mn(3)–Mn(1)	67.5(3)	O(2)–Mn(4)–O(7)	98.2(3)
O(4)–Mn(3)–Mn(1)	80.4(3)	O(31)–Mn(4)–O(7)	91.7(4)
N(3)–Mn(3)–Mn(1)	117.6(5)	O(2)–Mn(4)–N(6)	96.7(4)
N(1)–Mn(3)–Mn(1)	129.8(4)	O(31)–Mn(4)–N(6)	95.5(4)
N(2)–Mn(3)–Mn(1)	147.3(3)	O(7)–Mn(4)–N(6)	162.7(4)
O(1)–Mn(3)–O(21)	95.9(4)	O(2)–Mn(4)–N(5)	100.7(4)
O(1)–Mn(3)–O(4)	98.6(4)	O(31)–Mn(4)–N(5)	163.8(4)
O(21)–Mn(3)–O(4)	92.7(4)	O(7)–Mn(4)–N(5)	87.7(4)
O(1)–Mn(3)–N(3)	97.8(5)	N(6)–Mn(4)–N(5)	81.0(5)
O(21)–Mn(3)–N(3)	93.0(5)	O(2)–Mn(4)–N(4)	177.3(4)
O(4)–Mn(3)–N(3)	161.9(5)	O(31)–Mn(4)–N(4)	85.5(4)
O(1)–Mn(3)–N(1)	101.1(4)	O(7)–Mn(4)–N(4)	84.3(4)
O(21)–Mn(3)–N(1)	162.5(4)	N(6)–Mn(4)–N(4)	80.7(4)
O(4)–Mn(3)–N(1)	88.5(6)	N(5)–Mn(4)–N(4)	78.4(4)
N(3)–Mn(3)–N(1)	81.1(6)	Mn(3)–O(1)–Mn(2)	154.8(4)
O(1)–Mn(3)–N(2)	177.4(5)	Mn(3)–O(1)–Mn(1)	112.3(4)
O(21)–Mn(3)–N(2)	85.0(4)	Mn(2)–O(1)–Mn(1)	92.7(3)
O(4)–Mn(3)–N(2)	83.7(5)	Mn(4)–O(2)–Mn(1)	154.8(4)
N(3)–Mn(3)–N(2)	79.7(6)	Mn(4)–O(2)–Mn(2)	112.3(4)
N(1)–Mn(3)–N(2)	77.8(5)	Mn(1)–O(2)–Mn(2)	92.8(3)
Mn(1)···Mn(2)	2.844(2)	Mn(2)···Mn(3)	3.738(2)
Mn(1)···Mn(3)	3.191(3)	Mn(2)···Mn(4)	3.186(2)
Mn(1)···Mn(4)	3.737(2)	Mn(3)···Mn(4)	6.070(2)

Structures of Complexes **5**, **6** and **8**

The molecular geometry and the atom-labelling scheme of the cation of **5** are shown in Figure 3. The structure consists of a discrete monocationic tetranuclear unit having a twofold rotation axis. Selected interatomic distances and angles are listed in Table 3. The cation possesses a “butterfly” $[\text{Fe}_2(\mu_3\text{-O})_2\text{Mn}_2]$ core. Mn(1) and Mn(1a) occupy “body” positions, and Fe(1) and Fe(1a) occupy the “wing-tip” positions, with O(1) and O(1a) triply bridging each FeMn_2 wing. The structure can thus be considered as two edge-sharing FeMn_2O triangular units with a dihedral angle of 145.1°. In contrast to the Mn_4O_2 complex **3**, O(1) lies significantly out (0.14 Å) of the FeMn_2 plane. In addition to the two μ_3 -oxo groups, there are three bridging acetate groups in the tetranuclear structure, one each between the metal atom pairs Fe(1)Mn(1), Fe(1a)Mn(1a) and Mn(1)Mn(1a). Additionally, a salicylaldoximate dianion is

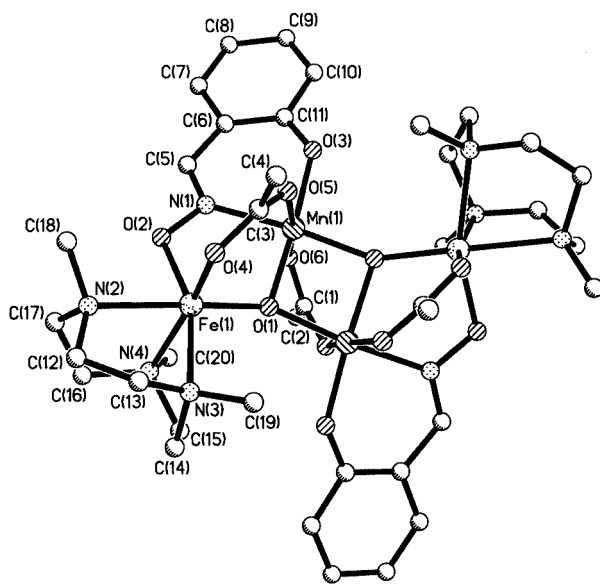


Figure 3. Molecular structure of the heterometal cation of **5**, showing the atom-numbering scheme

Table 3. Selected bond lengths [Å] and angles [°] for **5**

Fe(1)–O(1)	1.8795(13)
Fe(1)–O(2)	1.974(2)
Fe(1)–O(4)	1.989(2)
Fe(1)–N(4)	2.184(2)
Fe(1)–N(3)	2.230(2)
Fe(1)–N(2)	2.279(2)
Mn(1)–O(3)	1.897(2)
Mn(1)–O(1)#1	1.9343(13)
Mn(1)–O(1)	1.9397(14)
Mn(1)–N(1)	2.047(2)
Mn(1)–O(6)	2.160(2)
Mn(1)–O(5)	2.212(2)
O(1)–Fe(1)–O(2)	94.35(6)
O(1)–Fe(1)–O(4)	97.72(6)
O(2)–Fe(1)–O(4)	98.21(7)
O(1)–Fe(1)–N(4)	95.86(7)
O(2)–Fe(1)–N(4)	90.36(7)
O(4)–Fe(1)–N(4)	163.32(7)
O(1)–Fe(1)–N(3)	104.06(6)
O(2)–Fe(1)–N(3)	160.08(6)
O(4)–Fe(1)–N(3)	86.95(7)
N(4)–Fe(1)–N(3)	80.37(8)
O(1)–Fe(1)–N(2)	174.17(7)
O(2)–Fe(1)–N(2)	83.35(6)
O(4)–Fe(1)–N(2)	87.93(7)
N(4)–Fe(1)–N(2)	78.83(7)
N(3)–Fe(1)–N(2)	77.60(7)
O(3)–Mn(1)–O(1)#1	98.03(6)
O(3)–Mn(1)–O(1)	175.73(6)
O(1)#1–Mn(1)–O(1)	84.90(6)
O(3)–Mn(1)–N(1)	87.31(7)
O(1)#1–Mn(1)–N(1)	173.94(6)
O(1)–Mn(1)–N(1)	89.94(6)
O(3)–Mn(1)–O(6)	89.96(7)
O(1)#1–Mn(1)–O(6)	91.35(6)
O(1)–Mn(1)–O(6)	93.09(6)
N(1)–Mn(1)–O(6)	85.76(6)
O(3)–Mn(1)–O(5)	89.86(6)
O(1)#1–Mn(1)–O(5)	95.11(6)
O(1)–Mn(1)–O(5)	86.78(6)
N(1)–Mn(1)–O(5)	87.74(6)
O(6)–Mn(1)–O(5)	173.50(6)
O(3)–Mn(1)–Mn(1)#1	140.19(5)
O(1)#1–Mn(1)–Mn(1)#1	43.57(4)
O(1)–Mn(1)–Mn(1)#1	43.41(4)
N(1)–Mn(1)–Mn(1)#1	130.59(5)
O(6)–Mn(1)–Mn(1)#1	82.49(4)
O(5)–Mn(1)–Mn(1)#1	101.73(4)
Fe(1)–O(1)–Mn(1)#1	152.41(8)
Fe(1)–O(1)–Mn(1)	112.39(7)
Mn(1)#1–O(1)–Mn(1)	93.02(6)
Mn(1)···Mn(1a)	2.811(1)
Mn(1)···Fe(1)	3.174(1)
Fe(1)···Fe(1a)	6.022(1)
Fe(1)···Mn(1a)	3.704(1)

coordinated to Mn(1) through its phenolate oxygen atom O(3) and oxime nitrogen atom N(1), thus making Mn(1) six-coordinate. The X-ray structure clearly shows that the “body” metal ions are Jahn–Teller-distorted, high-spin d^4 Mn^{III} ions; the axially elongated sites are occupied by the carboxylate oxygen atoms of acetate, with Mn(1)–O(6) 2.160(2) Å, Mn(1)–O(5) 2.212(2) Å and O(5)–Mn(1)–O(6) 173.5°. Interestingly, the Mn(1)–O(1) distance [1.940(1) Å] is significantly shorter than the corres-

ponding bond length in the analogous cation of **6**, but is similar to that in **8**.

The coordination geometry of the “wing-tip” ferric ion Fe(1) is distorted octahedral, with three nitrogen atoms from the facially coordinated tridentate macrocyclic amine (L) and three oxygen atoms [O(2) from the deprotonated oxime group, O(4) from the bridging acetate and O(1) from the μ_3 -bridging oxo group], resulting in a *fac*- FeN_3O_3 coordination sphere. The Fe(1)–N(2) distance [2.279(2) Å] is significantly longer than the other Fe–N distances, due to the *trans* effect. The Fe–N (average 2.23 Å) and Fe–O (average 1.95 Å) distances are in agreement with a d^5 high-spin electronic configuration for the iron centres. The Fe(1)– μ_3 -oxo distance [1.880(1) Å] is, as expected, the shortest amongst the metal–ligand bond lengths. The iron atom Fe(1) is displaced by 0.28 Å from the mean basal plane comprising N(3)N(4)O(2)O(4) toward the apical μ_3 -oxygen atom O(1).

The structure of the cation of complex **6** is presented in Figure 4. The cation possesses an $\text{Fe}_2^{\text{III}}\text{Mn}_2^{\text{III}}(\mu_3\text{-O})_2$ core very similar to those present in the Fe_4O_2 (**1**), Mn_4O_2 (**3**) and $\text{Fe}_2\text{Mn}_2\text{O}_2$ (**5** and **8**) core structures. The metal centres are thus disposed in a “butterfly” arrangement based on two edge-sharing $\text{FeMn}_2(\mu_3\text{-O})$ triangular units, with the oxygen atoms O(1) and O(2) slightly above (0.07 Å) and below (0.02 Å) the Mn_2Fe triangle, as depicted below; note that the drawing is not meant to suggest a stepwise assembly process.

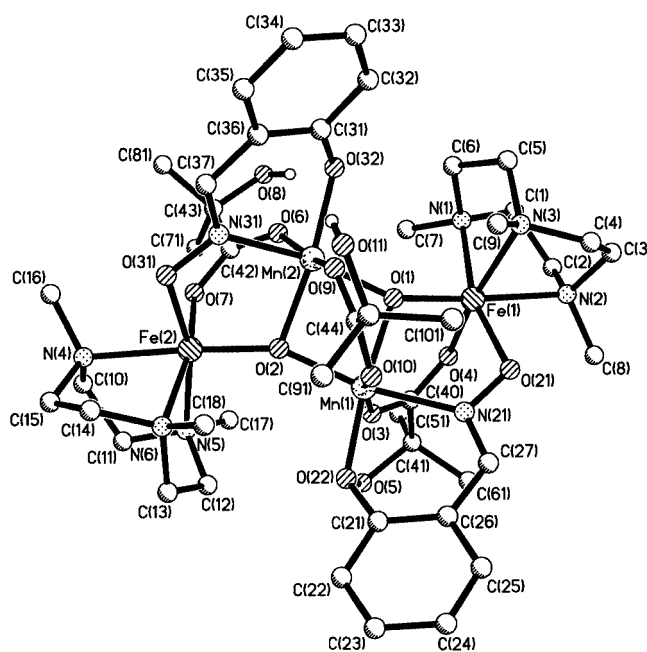
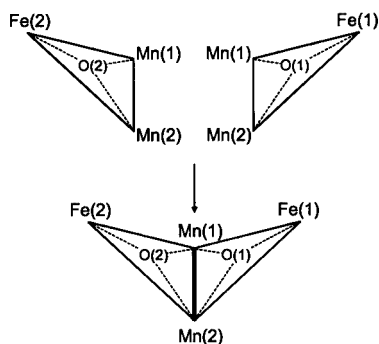


Figure 4. Structure of the tetranuclear monocation of **6**; phenyl rings (Ph) of the bridging diphenylglycolate (benzilate) $\text{Ph}_2\text{C}(\text{OH})\text{COO}^-$ are denoted by C atoms



The dispositions of the μ_3 -oxo groups are not completely symmetrical, but are consistent with all metal atoms being in the 3+ oxidation state. The dihedral angle between the planes Mn(1)Mn(2)Fe(2) and Mn(1)Mn(2)Fe(1) is 145.9°. Selected bond lengths and angles for the $\text{Fe}_2^{\text{III}}\text{Mn}_2^{\text{III}}\text{O}_2$ core and for the rest of the cation are given in Table 4. The “body” metal centres [Mn(1) and Mn(2)] show clear evidence of Jahn–Teller distortions, as expected for high-spin octahedral d^4 Mn^{III} , and the axially elongated sites are all occupied by carboxylate oxygen atoms of diphenylglycolic acid [O(3), O(10) for Mn(1) and O(6), O(9) for Mn(2)]. The hydroxy oxygen atoms of $(\text{C}_6\text{H}_5)_2\text{C}(\text{OH})\text{COO}^-$ [O(8), O(5) and O(11)] are not coordinated to any of the metal centres. There are three types of independent Fe–O distances, ranging from 1.863(2) to 2.045(2) Å, with the shortest, as expected, being the Fe– μ_3 -oxo distances Fe(1)–O(1) [1.863(2) Å] and Fe(2)–O(2) [1.876(2) Å]. The Fe–N distances *trans* to the μ_3 -oxo groups [Fe(1)–N(2) = 2.268(3) Å, Fe(2)–N(4) = 2.270(2) Å] are longer than the other Fe–N distances, due to the *trans* effect. The coordination geometry of the “wing-tip” ferric ions, Fe(1) and Fe(2), is distorted octahedral, with three nitrogen atoms from the facially coordinated tridentate macrocyclic amine (L) and three oxygen atoms [O(31) or O(21) of the deprotonated oxime group, O(4) or O(7) of the bridging carboxylate and O(1) or O(2) of the μ_3 -bridging oxo group] resulting in a *fac*- FeN_3O_3 coordination sphere. The Fe–N [average 2.20(6) Å] and Fe–O [average 1.95(6) Å] distances are similar to literature values^[28] for high-spin Fe^{III} complexes with this macrocyclic amine. A deviation from the idealised octahedral geometry at the metal centre is found for the ligand L; the N–Fe–N angles range from 77.6 to 81.2°, whereas the O–Fe–O angles fall between 91.7 and 98.2°. The iron ions Fe(1) and Fe(2) are displaced by 0.28 Å from the mean basal planes comprising O(21)O(4)N(3)N(1) and N(5)N(6)O(7)O(31), respectively, toward the apical μ_3 -oxygen atoms O(1) and O(2).

The “body” manganese ions, Mn(1) and Mn(2), are bridged by two oxo groups, O(2) and O(1). Each Mn is coordinated to three oxygen atoms [O(1), O(2) and phenolate O(22) or O(32)] and an imine nitrogen atom [N(21) or N(31)] of an oxime group in the basal plane. The carboxylate oxygen atoms O(3)/O(10) or O(6)/O(9) occupy the axially elongated apical positions. The Mn–N and Mn–O bond lengths are consistent with a d^4 high-spin electronic configuration for the Mn^{III} centres. The mangan-

Table 4. Selected bond lengths [Å] and angles [°] for **6**

Mn(1)–O(22)	1.906(2)	Fe(1)–O(1)	1.863(2)
Mn(1)–O(2)	1.930(2)	Fe(1)–O(21)	1.933(2)
Mn(1)–O(1)	1.972(2)	Fe(1)–O(4)	2.041(2)
Mn(1)–O(3)	2.097(2)	Fe(1)–N(3)	2.167(3)
Mn(1)–O(10)	2.103(2)	Fe(1)–N(1)	2.188(2)
Mn(1)–N(21)	2.113(2)	Fe(1)–N(2)	2.268(3)
Mn(1)–Mn(2)	2.8310(6)	Fe(2)–O(2)	1.876(2)
Mn(2)–O(32)	1.907(2)	Fe(2)–O(31)	1.931(2)
Mn(2)–O(1)	1.944(2)	Fe(2)–O(7)	2.045(2)
Mn(2)–O(2)	1.966(2)	Fe(2)–N(6)	2.149(2)
Mn(2)–N(31)	2.098(2)	Fe(2)–N(5)	2.205(2)
Mn(2)–O(9)	2.114(2)	Fe(2)–N(4)	2.270(2)
Mn(2)–O(6)	2.127(2)		
O(22)–Mn(1)–O(2)	103.93(8)	O(1)–Fe(1)–O(21)	95.68(8)
O(22)–Mn(1)–O(1)	172.69(8)	O(1)–Fe(1)–O(4)	97.72(8)
O(2)–Mn(1)–O(1)	83.21(7)	O(21)–Fe(1)–O(4)	93.00(9)
O(22)–Mn(1)–O(3)	86.86(8)	O(1)–Fe(1)–N(3)	96.82(10)
O(2)–Mn(1)–O(3)	96.82(8)	O(21)–Fe(1)–N(3)	92.73(10)
O(1)–Mn(1)–O(3)	90.74(8)	O(4)–Fe(1)–N(3)	163.75(10)
O(22)–Mn(1)–O(10)	85.02(8)	O(1)–Fe(1)–N(1)	100.61(9)
O(2)–Mn(1)–O(10)	95.00(8)	O(21)–Fe(1)–N(1)	163.08(9)
O(1)–Mn(1)–O(10)	96.05(8)		
O(3)–Mn(1)–O(10)	166.98(8)	O(4)–Fe(1)–N(1)	89.38(10)
O(22)–Mn(1)–N(21)	85.82(9)	N(3)–Fe(1)–N(1)	80.85(11)
O(2)–Mn(1)–N(21)	169.12(8)	O(1)–Fe(1)–N(2)	176.44(9)
O(1)–Mn(1)–N(21)	87.21(8)	O(21)–Fe(1)–N(2)	85.53(9)
O(3)–Mn(1)–N(21)	88.42(8)	O(4)–Fe(1)–N(2)	85.54(10)
O(10)–Mn(1)–N(21)	80.86(9)	N(3)–Fe(1)–N(2)	79.77(11)
O(22)–Mn(1)–Mn(2)	143.91(6)	N(1)–Fe(1)–N(2)	77.95(10)
O(2)–Mn(1)–Mn(2)	43.89(5)	O(2)–Fe(2)–O(31)	95.65(8)
O(1)–Mn(1)–Mn(2)	43.30(5)	O(2)–Fe(2)–O(7)	98.24(8)
O(3)–Mn(1)–Mn(2)	109.38(6)	O(31)–Fe(2)–O(7)	91.73(8)
O(10)–Mn(1)–Mn(2)	83.00(5)	O(2)–Fe(2)–N(6)	95.98(8)
N(21)–Mn(1)–Mn(2)	125.31(6)	O(31)–Fe(2)–N(6)	95.43(8)
O(32)–Mn(2)–O(1)	103.88(8)	O(7)–Fe(2)–N(6)	163.37(8)
O(32)–Mn(2)–O(2)	172.94(8)	O(2)–Fe(2)–N(5)	101.08(8)
O(1)–Mn(2)–O(2)	83.02(7)	O(31)–Fe(2)–N(5)	163.17(8)
O(32)–Mn(2)–N(31)	86.14(9)	O(7)–Fe(2)–N(5)	87.65(8)
O(1)–Mn(2)–N(31)	166.16(8)	O(6)–Fe(2)–N(5)	81.16(9)
O(2)–Mn(2)–N(31)	86.81(8)	O(2)–Fe(2)–N(4)	175.81(8)
O(32)–Mn(2)–O(9)	83.73(8)	O(31)–Fe(2)–N(4)	85.60(8)
O(1)–Mn(2)–O(9)	91.94(8)	O(7)–Fe(2)–N(4)	85.71(8)
O(2)–Mn(2)–O(9)	94.70(8)	N(6)–Fe(2)–N(4)	79.91(9)
N(31)–Mn(2)–O(9)	79.53(8)	N(5)–Fe(2)–N(4)	77.58(8)
O(32)–Mn(2)–O(6)	88.20(8)		
O(1)–Mn(2)–O(6)	100.22(7)	Fe(1)–O(1)–Mn(2)	154.88(10)
O(2)–Mn(2)–O(6)	92.03(7)	Fe(1)–O(1)–Mn(1)	112.26(9)
N(31)–Mn(2)–O(6)	89.47(8)	Mn(2)–O(1)–Mn(1)	92.62(8)
O(9)–Mn(2)–O(6)	166.74(8)	Fe(2)–O(2)–Mn(1)	154.95(10)
O(32)–Mn(2)–Mn(1)	142.84(6)	Fe(2)–O(2)–Mn(2)	111.80(9)
O(1)–Mn(2)–Mn(1)	44.08(5)	Mn(1)–O(2)–Mn(2)	93.21(8)
O(2)–Mn(2)–Mn(1)	42.90(5)		
N(31)–Mn(2)–Mn(1)	122.91(6)		
O(9)–Mn(2)–Mn(1)	80.11(5)		
O(6)–Mn(2)–Mn(1)	112.36(5)		
Mn(1)···Mn(2)	2.831(1)	Mn(2)···Fe(1)	3.715(1)
Mn(1)···Fe(1)	3.185(1)	Mn(2)···Fe(2)	3.182(1)
Mn(1)···Fe(2)	3.716(1)	Fe(2)···Fe(1)	6.048(1)

ese centres Mn(1) and Mn(2) lie out of the best basal planes comprising Mn(1)N(21)O(22)O(1)O(2) and Mn(2)N(31)O(32)O(1)O(2) by 0.028 Å and 0.09 Å in the direction of the bridging O(3) or O(6), respectively.

The structure of **8**·2CH₃CN is very similar to that of **5** and **6** and hence only the core structure is shown in Fig-

ure 5. Table 5 gives selected bond lengths and angles for **8**. Remarkably, the Mn–O–Mn angles in **5**, **6** and **8** (93°) are nearly identical. On the other hand, the Mn– μ_3 -O distances in **8** (average 1.92 Å) are shorter than those in **5** or **6** (average 1.94 Å), although the Fe– μ_3 -O distances for **5**, **6** and **8** are nearly identical (average 1.88 Å). This difference in bond lengths presumably has significant effects on the ground state S_t values, as will be shown later.

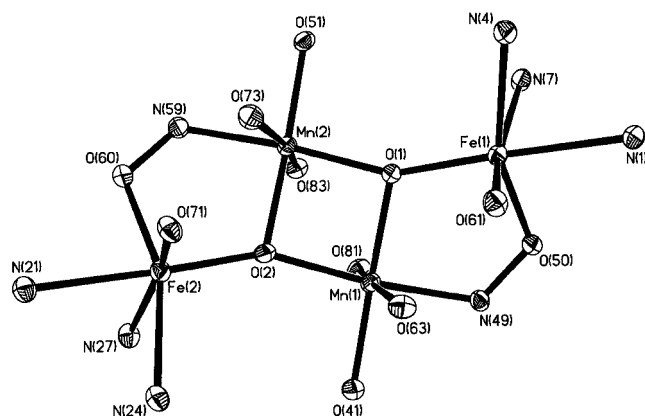


Figure 5. Atom connectivity of the $\text{Fe}_2\text{Mn}_2\text{O}_2$ core in the cation of **8**

Mössbauer Spectroscopy

The Mössbauer spectra of **1** (Figure 6, curve A) and **2** were recorded without an applied field at 80 K. Each spectrum is best fit to two equal-area doublets, whose isomer shifts (δ_{Fe}) and quadrupole splitting (ΔE_Q) values are listed in Table 6. The two doublets imply two Fe sites with different coordination spheres, in agreement with the molecular structure of **1**, and are thus assigned to the “body” and “wing-tip” pairs of Fe^{III} atoms. The isomer shift δ_{Fe} of 0.5 ± 0.05 mm/s is of the magnitude expected for the high-spin ferric state and is close to the values reported for similar compounds.^[30] The ΔE_Q values for both sites in **1** and **2** reflect deviations from octahedral geometry, since the valence electron contribution to ΔE_Q is negligible for high-spin Fe^{III} . The two ΔE_Q values are significantly different, and larger than the 0.4–0.7 mm/s range observed for basic iron carboxylates.^[31] By comparing the bond lengths for the NO_5 coordination sphere around Fe(1) and Fe(2) with those of the more symmetrical N_3O_3 coordination sphere about Fe(3) and Fe(4), the doublet with $\Delta E_Q \approx 1.37$ mm/s can be assigned to the “body” iron atoms Fe(1) and Fe(2), whereas the inner doublet is assignable to the “wing-tip” iron atoms Fe(3) and Fe(4). This assignment is also corroborated by the Mössbauer data for complexes **5–10**.

The powder-state Mössbauer spectrum of **6** at 80 K is displayed in Figure 6, curve B. Essentially similar spectra were obtained for the remaining complexes of the group. The δ_{Fe} and ΔE_Q values for **5–10** are listed in Table 6. Mössbauer results indicate a single quadrupole splitting, in accordance with only one type of iron coordination sphere

Table 5. Selected bond lengths [Å] and angles [$^\circ$] for **8**

Fe(1)–O(1)	1.892(2)	Mn(1)–O(41)	1.890(2)
Fe(1)–O(50)	1.959(2)	Mn(1)–O(2)	1.927(2)
Fe(1)–O(61)	2.013(2)	Mn(1)–O(1)	1.933(2)
Fe(1)–N(7)	2.190(2)	Mn(1)–N(49)	2.022(2)
Fe(1)–N(4)	2.226(2)	Mn(1)–O(81)	2.187(2)
Fe(1)–N(1)	2.265(2)	Mn(1)–O(63)	2.222(2)
Fe(1)–O(2)	1.895(2)	Mn(1)–Mn(2)	2.8034(6)
Fe(1)–O(60)	1.961(2)	Mn(2)–O(51)	1.890(2)
Fe(1)–O(71)	1.985(2)	Mn(2)–O(1)	1.917(2)
Fe(1)–N(27)	2.196(2)	Mn(2)–O(2)	1.918(2)
Fe(1)–N(24)	2.213(2)	Mn(2)–N(59)	2.010(2)
Fe(1)–N(21)	2.268(2)	Mn(2)–O(83)	2.220(2)
		Mn(2)–O(73)	2.294(2)
O(1)–Fe(1)–O(50)	93.52(8)	O(41)–Mn(1)–O(2)	96.86(8)
O(1)–Fe(1)–O(61)	96.42(7)	O(41)–Mn(1)–O(1)	176.12(8)
O(50)–Fe(1)–O(61)	100.55(8)	O(2)–Mn(1)–O(1)	84.03(7)
O(1)–Fe(1)–N(7)	97.14(8)	O(41)–Mn(1)–N(49)	88.70(8)
O(50)–Fe(1)–N(7)	92.00(8)	O(2)–Mn(1)–N(49)	171.68(8)
O(61)–Fe(1)–N(7)	160.89(8)	O(1)–Mn(1)–N(49)	90.84(8)
O(1)–Fe(1)–N(4)	106.76(8)	O(41)–Mn(1)–O(81)	89.73(8)
O(50)–Fe(1)–N(4)	158.64(8)	O(2)–Mn(1)–O(81)	91.01(7)
O(61)–Fe(1)–N(4)	84.10(8)	O(1)–Mn(1)–O(81)	94.04(7)
N(7)–Fe(1)–N(4)	79.13(8)	N(49)–Mn(1)–O(81)	82.80(8)
O(1)–Fe(1)–N(1)	173.57(8)	O(41)–Mn(1)–O(63)	87.97(7)
O(50)–Fe(1)–N(1)	81.35(8)	O(2)–Mn(1)–O(63)	96.89(7)
O(61)–Fe(1)–N(1)	88.36(8)	O(1)–Mn(1)–O(63)	88.17(7)
N(7)–Fe(1)–N(1)	79.27(8)	N(49)–Mn(1)–O(63)	89.47(8)
N(4)–Fe(1)–N(1)	77.94(8)	O(81)–Mn(1)–O(63)	171.98(7)
O(2)–Fe(2)–O(60)	93.89(8)	O(51)–Mn(2)–O(1)	97.49(7)
O(2)–Fe(2)–O(71)	96.96(8)	O(51)–Mn(2)–O(2)	177.81(8)
O(60)–Fe(2)–O(71)	98.69(8)	O(1)–Mn(2)–O(2)	84.70(7)
O(2)–Fe(2)–N(27)	96.72(8)	O(51)–Mn(2)–N(59)	87.71(8)
O(60)–Fe(2)–N(27)	90.30(8)	O(1)–Mn(2)–N(59)	174.32(8)
O(71)–Fe(2)–N(27)	163.06(8)	O(2)–Mn(2)–N(59)	90.10(8)
O(2)–Fe(2)–N(24)	105.74(8)	O(51)–Mn(2)–O(83)	89.21(7)
O(60)–Fe(2)–N(24)	158.95(8)	O(1)–Mn(2)–O(83)	93.75(7)
O(71)–Fe(2)–N(24)	86.61(8)	O(2)–Mn(2)–O(83)	90.68(7)
N(27)–Fe(2)–N(24)	80.09(8)	N(59)–Mn(2)–O(83)	84.02(8)
O(2)–Fe(2)–N(21)	173.58(8)	O(51)–Mn(2)–O(73)	91.50(7)
O(60)–Fe(2)–N(21)	81.18(8)	O(1)–Mn(2)–O(73)	95.73(7)
O(71)–Fe(2)–N(21)	87.89(8)	O(2)–Mn(2)–O(73)	88.24(7)
N(27)–Fe(2)–N(21)	79.29(8)	N(59)–Mn(2)–O(73)	86.36(8)
N(24)–Fe(2)–N(21)	78.66(8)	O(83)–Mn(2)–O(73)	170.32(7)
Fe(1)–O(1)–Mn(2)	154.22(10)		
Fe(1)–O(1)–Mn(1)	111.25(8)		
Mn(2)–O(1)–Mn(1)	93.49(7)		
Fe(2)–O(2)–Mn(2)	112.25(9)		
Fe(2)–O(2)–Mn(1)	150.98(10)		
Mn(2)–O(2)–Mn(1)	93.64(8)		
Mn(1)···Mn(2)	2.803(1)	Mn(2)···Fe(1)	3.713(2)
Mn(1)···Fe(1)	3.157(2)	Mn(2)···Fe(2)	3.166(2)
Mn(1)···Fe(2)	3.700(2)	Fe(2)···Fe(1)	6.024(2)

in the solid-state structure, namely the “wing-tip” iron sites Fe(1) and Fe(2). The δ_{Fe} values of ca. 0.45 mm/s are consistent with a d^5 high-spin electron configuration for the iron centres Fe(1) and Fe(2) in complexes **5–10**. The isomer shift values are surprisingly constant within these complexes, and indicate that a change in the carboxylate group – with its varying electron-withdrawing power – has little effect upon the s-electron density at the iron nucleus. The ΔE_Q values (0.53–0.61 mm/s) for **5–10** lie within the 0.4–0.7 mm/s range found for basic iron carboxylates, and are similar to those for analogous structures with a dis-

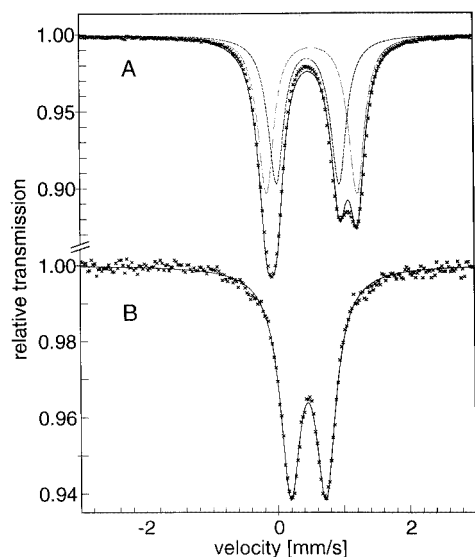
Figure 6. Mössbauer spectra of **1** (A) and **6** (B) at 80 K

Table 6. Mössbauer parameters at 80 K

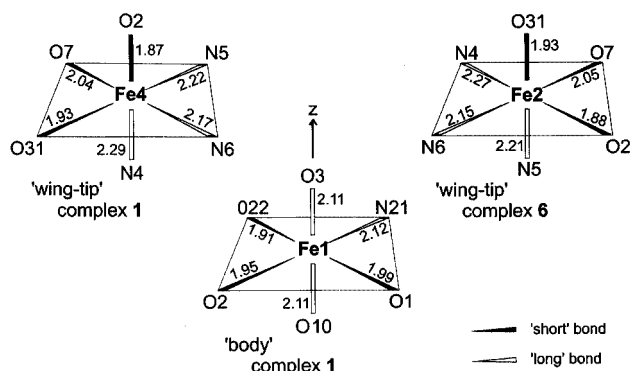
Complex	δ_{Fe} [mm·s ⁻¹] ^[a]	ΔE_Q [mm·s ⁻¹]
1	0.47	0.95
	0.53	1.37
2	0.47	0.95
	0.53	1.38
5	0.45	0.61
6	0.46	0.54
7	0.45	0.53
8	0.46	0.58
9	0.46	0.54
10	0.46	0.54

^[a] Isomer shift relative to iron foil at room temperature. Typical errors are ± 0.01 for δ_{Fe} and ± 0.02 for ΔE_Q .

torted octahedral symmetry. Comparison of the Mössbauer data for **5–10** with those for **1** and **2** makes it clear that the “wing-tip” positions in complexes **5–10** are occupied by Fe atoms in all cases, and hence the cyclic amine 1,4,7-trimethyl-1,4,7-triazacyclononane is coordinated to iron centres only. This is confirmed by the X-ray structures of **5**, **6** and **8**.

The remarkable difference in quadrupole splitting of the “wing-tip” and “body” iron sites in complexes **1**, **2** and **6** can be rationalised by comparing the distributions of bond lengths for the different coordination polyhedra. To this end, the iron–ligand bonds were classified into “short” and “long” bonds as sketched in Scheme 1.

It is striking that for the “wing-tip” iron atoms, the three shortest Fe–O bonds lie in a *fac* configuration, whereas for the “body” site, they have a *mer* arrangement. Thus, the “body” site can be regarded as a distorted octahedron with bond compression in the equatorial plane (if the *z* axis is taken in the O3–Fe1–O10 direction). Since large quadrupole splittings of high-spin Fe^{III} (3d⁵ configuration) are the result of strong anisotropy in the covalent delocalisation of valence electrons, as suggested for the Fe–O–Fe unit in other systems,^[32] we infer that the large electric field gradi-

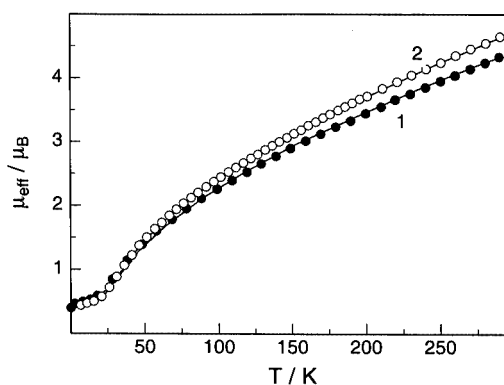


Scheme 1

ent for the “body” site [Fe(1) of complexes **1** and **2**] originates predominantly from strong covalency of the $d_{x^2-y^2}$ orbital and the resulting anisotropy in the distribution of valence electrons. In contrast, the short bonds in the “wing-tip” sites are distributed in a more balanced manner among the three major axes. In addition, the covalency due to the particularly short Fe4–O2 and Fe2–O2 bonds in compounds **1** and **6**, respectively, appears to be partly compensated for by a pronounced *trans* effect in the opposite bonds. Thus, the covalent delocalisation of 3d electrons seems to be more isotropic, as it affects both e_g orbitals. Since these orbitals, $d_{x^2-y^2}$ and d_{z^2} , have equally strong but opposite contributions to the total electric field gradient, the smaller quadrupole splittings observed for the “wing-tip” iron sites appears to be plausible.

Magnetic Properties

The magnetic susceptibility data for polycrystalline samples of **1–10** were collected in the temperature range 2–290 K in an applied magnetic field of 1 T and are displayed in Figures 7–9 as plots of the effective magnetic moment (μ_{eff}) versus temperature (*T*). Table 7 summarises the intracluster exchange parameters, together with the observed spin ground states, and selected μ_{eff} values for **1–10** are listed in Table 8. The solid lines in Figures 7–9 represent

Figure 7. Temperature dependence of the magnetic moments of complexes **1** and **2**; the solid lines represent the best fit of data to the Heisenberg–Dirac–van Vleck model (see text)

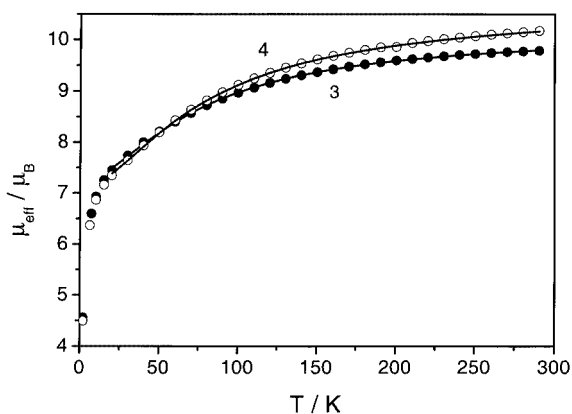


Figure 8. Plots of μ_{eff} vs. T for solid **3** and **4**; the solid lines are the best least-squares fits of the experimental data to the theoretical equation

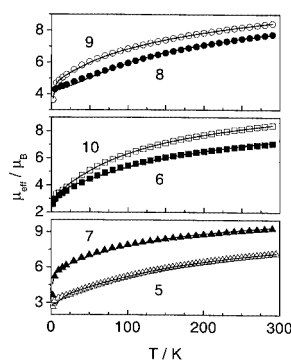


Figure 9. Temperature dependence of the magnetic moment, μ_{eff} , for **5–10**; the solid lines represent the simulation with the spin Hamiltonian (see text)

ent the simulations. The model used for the simulations involves two pairwise exchange interactions, J_{wb} for the wing-tip-body and J_{bb} for the body-body interactions. The oxide bridges have been shown to be more important mediators for the exchange interactions than the carboxylate bridges in the structurally related complexes [Fe₄(μ₃-O)₂]⁸⁺,^[3,4] [Mn₄(μ₃-O)₂]⁸⁺,^[9,35] [Cr₄(μ₃-O)₂]⁸⁺,^[33] [V₄(μ₃-O)₂]⁸⁺,^[34] [Cr₂(μ₃-O)₂Fe]⁸⁺,^[13] and [Cr₂(μ₃-O)₂Mn]⁸⁺,^[14] in which a similar “ $2J$ ” model is able to adequately describe the mag-

Table 8. Selected μ_{eff} values as a function of temperature for complexes **1–10**

Compound	Complex	μ_{eff} , μ_{B} (T [K])
1	Fe ₄ benzilate	0.56 (2), 1.26 (40), 2.46 (110), 4.32 (290)
2	Fe ₄ triphenyl acetate	0.52 (5), 1.30 (40), 2.64 (110), 4.66 (290), 4.76 (300)
3	Mn ₄ benzilate	4.56 (2), 6.93 (10), 8.00 (40), 9.07 (110), 9.79 (290)
4	Mn ₄ triphenyl acetate	4.50 (2), 6.87 (10), 7.95 (40), 9.27 (110), 10.22 (290)
5	Fe ₂ Mn ₂ acetate	2.67 (2), 3.14 (5), 3.38 (10), 3.49 (15), 4.05 (40), 5.37 (110), 7.13 (290), 7.16 (295)
6	Fe ₂ Mn ₂ benzilate	2.60 (2), 2.98 (5), 3.23 (15), 4.20 (40), 5.58 (110), 7.05 (290)
7	Fe ₂ Mn ₂ triphenyl acetate	3.63 (2), 5.20 (5), 5.95 (15), 6.79 (40), 8.01 (110), 9.27 (290)
8	Fe ₂ Mn ₂ benzoate	3.62 (2), 4.30 (5), 4.44 (10), 4.50 (15), 4.96 (40), 6.10 (110), 7.75 (290)
9	Fe ₂ Mn ₂ chloroacetate	3.63 (2), 5.06 (15), 5.82 (40), 6.97 (110), 8.42 (290)
10	Fe ₂ Mn ₂ propionate	2.72 (2), 3.62 (15), 4.73 (40), 6.49 (110), 8.39 (290)

netic behaviour of the tetranuclear complexes. Consequently, the other conceivable “ $3J$ ” model has not been considered to avoid overparametrisation.

The resulting spin Hamiltonian used to describe the isotropic exchange interactions is given by

$$\hat{H} = -2J_{\text{wb}} (\hat{S}_1 \cdot \hat{S}_3 + \hat{S}_2 \cdot \hat{S}_3 + \hat{S}_1 \cdot \hat{S}_4 + \hat{S}_2 \cdot \hat{S}_4) - 2J_{\text{bb}} (\hat{S}_1 \cdot \hat{S}_2)$$

where S_i ($i = 1, 2, 3, 4$) = $5/2$ for **1** and **2**, S_i ($i = 1, 2, 3, 4$) = 2 for **3** and **4**, and $S_1 = S_2 = 2$; $S_3 = S_4 = 5/2$ for **5–10**.

The magnetic moment for **1** and **2** decreases monotonically with decreasing temperature to an essentially diamag-

Table 7. Magnetic parameters for complexes **1–10**

Compound	Complex	J_{wb} [cm ⁻¹] ($J_{13} = J_{24} = J_{23} = J_{14}$)	J_{bb} [cm ⁻¹] (J_{12})	g ($g_1 = g_2 = g_3 = g_4$)	D [cm ⁻¹] ($D_1 = D_2 = D_3 = D_4$)	Ground state S_{T}
1	Fe ₄ benzilate	−41.4	0 (fixed)	2.0 (fixed)	—	0
2	Fe ₄ triphenyl acetate	−38.2	0 (fixed)	2.0 (fixed)	—	0
3	Mn ₄ benzilate	−0.47	−7.73	2.099 (fixed)	0 (fixed)	3
4	Mn ₄ triphenyl acetate	−1.63	−6.71	2.215 (fixed)	0 (fixed)	3
5	Fe ₂ Mn ₂ acetate	−25.2	−35.1	2.05 (fixed)	−0.38	1
6	Fe ₂ Mn ₂ benzilate	−22.3	−31.6	2.00 (fixed)	0 (fixed)	1
7	Fe ₂ Mn ₂ triphenyl acetate	−5.5	−10.2	2.00 (fixed)	0 (fixed)	2, 3
8	Fe ₂ Mn ₂ benzoate	−19.4	−28.9	2.09	0	2, 1
9	Fe ₂ Mn ₂ chloroacetate	−10.6	−17.8	2.01 (fixed)	2.07	2
10	Fe ₂ Mn ₂ propionate	−14.4	−19.4	2.13 (fixed)	0 (fixed)	1

netic value of $0.55 \mu_B$ for **1** at 2 K and $0.52 \mu_B$ at 5 K for **2**; the residual nonzero moment is due primarily to an amount of a paramagnetic impurity PI (assumed $S = 5/2$). Thus, the temperature-dependent behaviours of the magnetic moments of **1** and **2** clearly indicate an $S_t = 0$ electronic ground state, in agreement with previous observations^[1–6] for other molecules of similar structure. The theoretical van Vleck equation used for simulation of the susceptibility data has been described earlier.^[4]

The Zeeman interaction of the high-spin ferric ion in a 6A_1 ground state with practically no contribution from orbital angular momentum is isotropic and the observed g values are thus very close to the free-electron spin value of 2.0. Hence, we have used a fixed value of $g = 2.0$ for **1** and **2** during simulation. As the quality of the fit is negligibly dependent on J_{bb} ,^[3,4] we have kept $J_{bb} = 0$. Previous work has shown that J_{bb} cannot be precisely determined from the susceptibility data in the temperature range ca 4–300 K for such complexes, but J_{wb} can be evaluated with reasonable accuracy.^[3,4] Additionally, an error-surface plot for **1** as a function of J_{wb} and J_{bb} shows that, while the value of J_{wb} is well determined by the fitting procedure, the value of J_{bb} is not. The best fits are shown as solid lines in Figure 7 and the fitting parameters are $J_{wb} = -41.4 \text{ cm}^{-1}$, $J_{bb} = 0$ (fixed), $g = 2.0$ (fixed) and $PI = 0.008$ for **1**, and $J_{wb} = -38.2 \text{ cm}^{-1}$, $J_{bb} = 0$ (fixed), $g = 2.00$ (fixed) and $PI = 0.009$ for **2**. The J_{wb} values obtained compare closely with those previously determined by us for the Fe_4 acetate system^[4], and also those reported in the literature.^[3,6]

The effective magnetic moment of complexes **3** and **4** as a function of temperature is shown in Figure 8. The magnetic moment gradually decreases to $6.93 \mu_B$ at 10 K for **3** and $6.87 \mu_B$ at 10 K for **4**, whereupon the moment falls sharply to $4.56 \mu_B$ for **3** and $4.50 \mu_B$ for **4** by 2 K. Thus, the temperature-dependent behaviours of the magnetic moments of **3** and **4** suggest an $S_t = 3$ ground state. In both cases, only data for temperatures above 20 K were considered in the fit, to avoid complications at low temperature from zero-field splitting. The solid lines in Figure 8 represent the best fits with the following parameters: $J_{wb} = -0.47 \text{ cm}^{-1}$, $J_{bb} = -7.73 \text{ cm}^{-1}$, $g = 2.099$ (fixed) and $D = 0$ (fixed) for **3**, and $J_{wb} = -1.63 \text{ cm}^{-1}$, $J_{bb} = -6.71 \text{ cm}^{-1}$, $g = 2.215$ (fixed) and $D = 0 \text{ cm}^{-1}$ (fixed) for **4**. Field-dependent magnetisation measurements (not shown) at 2 K up to 6 T also confirm that the ground state for **3** is $S_t = 3$ [simulation with $S = 3.0$ (fixed), $g = 2.02$, $D = 4.13 \text{ cm}^{-1}$]. The ground state is within 5 cm^{-1} of the first excited state with $S_t = 4$.

We note that the g values employed for the simulation are high for Mn^{III} . Nevertheless, they do not affect our conclusion that **3** and **4** have an $S_t = 3$ ground state. The ground state of $S_t = 3$ has been found for all carboxylate-bridged clusters with an $[Mn_4O_2]^{8+}$ core except one with a quintuply degenerate ground state.^[35]

At 295 K the magnetic moment ($\mu_{eff}/\text{molecule}$) for **5** is $7.16 \mu_B$, which is significantly lower than the value of $\mu_{eff} = 10.86 \mu_B$ expected for an uncoupled system containing two Fe^{III} ($S = 5/2$) and two Mn^{III} ($S = 2$) ions. On lowering the temperature, μ_{eff} decreases monotonically until it reaches a

value of $\mu_{eff} = 2.67 \mu_B$ at 2 K, indicating a ground state of $S_t = 1$ (Figure 9). A full-matrix diagonalisation approach including spin exchange ($-2J S_1 \cdot S_2$), Zeeman interactions, and single-ion zero-field interaction (DS_z^2), was employed to fit the data. The solid line in Figure 9 shows the good quality of the fit above $T = 15 \text{ K}$ with the following parameters:

$J_{FeMn} = J_{wb} = -25.2 \text{ cm}^{-1}$; $J_{MnMn} = J_{bb} = -35.1 \text{ cm}^{-1}$; $D(Mn^{III}) = -0.38 \text{ cm}^{-1}$ and $g = 2.05$ (fixed). As it is difficult, if not impossible, to unambiguously determine the sign of D from powder magnetic susceptibility measurements, one should not put too much weight on the absolute value of D , although inclusion of D as a parameter slightly improved the quality of the fit. We addressed the point of global and local minima by consideration of the two-dimensional contour projection of the error surface. The error surface shows that the fitting procedure has correctly identified the global minimum and we conclude that **5** has an $S_t = 1$ ground state lying 22.3 cm^{-1} below the first excited state with $S_t = 2$. For a system of two high-spin Fe^{III} and two high-spin Mn^{III} ions disposed in a butterfly-type arrangement as found in complexes **5–10**, the overall spin degeneracy (900) is distributed over 110 levels with S_t values ranging from 0 to 9.

The effective magnetic moment ($\mu_{eff}/\text{molecule}$) for **6** decreases monotonically with decreasing temperature from $7.05 \mu_B$ at 290 K to $2.60 \mu_B$ at 2 K (Figure 9). The two exchange coupling constants, J_{wb} and J_{bb} , were allowed to vary independently in the full-matrix diagonalisation program to optimise the agreement. A good fit was found with the following parameters: $J_{wb} = J_{FeMn} = -22.3 \text{ cm}^{-1}$, $J_{bb} = J_{MnMn} = -31.6 \text{ cm}^{-1}$, $g = 2.0$ (fixed) and $D = 0$ (fixed). The ground state of $S_t = 1$ for **6** lies about 14 cm^{-1} below the first excited state with $S_t = 2$.

A steady decrease of the magnetic moment with decreasing temperature is observed for **7**. The value of μ_{eff} at 2 K ($3.63 \mu_B$) clearly indicates a different ground state than that for **5** or **6** with $S_t = 1$. The solid line in Figure 9 shows the good quality of the fit with the following parameters: $J_{wb} = J_{FeMn} = -5.5 \text{ cm}^{-1}$; $J_{bb} = J_{MnMn} = -10.16 \text{ cm}^{-1}$; $g = 2.00$ (fixed) and $D = 0$ (fixed). The relative error surface for fitting the magnetic data of **7** as a function of both J_{FeMn} and J_{MnMn} , representing a well-defined global minimum in the parameter space, has allowed us to estimate the error bars on the quoted J_{FeMn} and J_{MnMn} values as approximately ± 0.2 and $\pm 1.0 \text{ cm}^{-1}$, respectively. The ground state of $S_t = 2$ for **7** obtained from the exchange coupling constants is separated from the first excited state with $S_t = 3$ by an energy gap of only 5 cm^{-1} .

A good fit of the magnetic data for **8** yields $J_{wb} = J_{FeMn} = -19.38 \text{ cm}^{-1}$, $J_{bb} = J_{MnMn} = -28.91 \text{ cm}^{-1}$, $g = 2.09$ and $D = 0$ (Figure 9). The ground state of $S_t = 1$ for **8** is not well separated ($\Delta E \approx 1 \text{ cm}^{-1}$) from the first excited state with $S_t = 2$.

The magnetic behaviour of **9** can be easily interpreted in terms of the competing influence of J_{wb} and J_{bb} upon spin coupling, yielding a ground state of $S_t = 2$. An excellent fit representing a well-defined global minimum for **9**, together

with the experimental magnetic moments, is shown in Figure 9. The parameters used for the least-squares fitting (fit shown as a solid line in Figure 9) are $J_{\text{wb}} = J_{\text{FeMn}} = -10.6 \text{ cm}^{-1}$, $J_{\text{bb}} = J_{\text{MnMn}} = -17.8 \text{ cm}^{-1}$, $g = 2.01$ (fixed) and $D = 2.07 \text{ cm}^{-1}$ (fixed). The relative error surface calculation has allowed us to estimate the error bars on the J_{FeMn} and J_{MnMn} values as approximately $\pm 0.6 \text{ cm}^{-1}$ and $\pm 1.5 \text{ cm}^{-1}$, respectively. The relatively large uncertainties in the absolute magnitudes of J_{FeMn} and J_{MnMn} do not affect our conclusion that **9** has an $S_t = 2$ ground state lying 15.8 cm^{-1} below the first excited state of $S_t = 1$.

For **10**, a monotonous decrease of the magnetic moment with decreasing temperature, reaching a value of $\mu_{\text{eff}} = 2.72 \mu_{\text{B}}$ at 2 K, is observed. This clearly indicates a ground state with $S_t > 1$, which is attained by competing antiferromagnetic coupling between the wing-body ($J_{\text{wb}} = -14.4 \text{ cm}^{-1}$) and the body-body ($J_{\text{bb}} = -19.4 \text{ cm}^{-1}$) metal centres. The g value used for the simulation of the experimental data (data shown as squares in Figure 9) is $g = 2.13$. The solid line in Figure 9 is the simulation of the magnetic data with the abovementioned parameters. The evaluated lowest lying state of $S_t = 1$ lies 18 cm^{-1} below the second lowest state with $S_t = 2$.

Discussion

In the preceding section it has been experimentally established that **1** and **2**, with the Fe_4O_2 core, possess an $S_t = 0$ ground state. All thermally populated excited states are effectively only determined by J_{wb} , and the intrinsic character (i.e. antiparallel coupling) of the $\text{Fe}(2) \cdots \text{Fe}(1)$ interaction, $J_{\text{bb}} = J_{12}$, can be totally negated due to spin frustration,^[20] making the J_{bb} interaction indeterminate in the $[\text{Fe}_4(\mu_3\text{-O})_2]^{8+}$ core. On the other hand, **3** and **4**, with the Mn_4O_2 core, possess the ground state $S_t = 3$, irrespective of the nature of the bridging carboxylate, as has been found earlier.^[9] In contrast, variation of the six bridging carboxylates from acetate (**5**), to benzoate (diphenylglycolate) (**6**), triphenyl acetate (**7**), benzoate (**8**), chloroacetate (**9**), and propionate (**10**), causes changes in the ground states for **5–10**, varying from $S_t = 1$ to 3, although the replacement of acetate in **5** by benzoate in **6** or benzoate in **8** has little structural effect within the $[\text{Fe}_2\text{Mn}_2\text{O}_2]^{8+}$ core, as is evident from the X-ray structures. These ground states have been confirmed by the field-dependent (0.5–6.5 T) magnetisation measurements. This indicates that the “*R*” groups of the different carboxylic acids (RCOOH) might not be that innocent in mediating exchange interactions, as is commonly taken for granted. The ground state does not represent the smallest spin state possible for the electronic d^n configuration when both interactions are antiferromagnetic. It is noteworthy in this respect that the ratio of competing coupling pathways, and not so much their absolute magnitudes, determines the electronic structures of these butterfly complexes. The ratio $J_{\text{MnMn}}/J_{\text{FeMn}}$ varies from 1.39 for **5** (acetate), to 1.42 for **6** (benzoate), 1.85 for **7** (triphenyl acetate), 1.49 for **8** (benzoate), 1.68 for **9** (chloroacetate), and 1.35

for **10** (propionate). Figure 10 gives a selective spin-correlation diagram for the $\text{Fe}_2^{\text{III}}\text{Mn}_2^{\text{III}}(\text{O})_2$ butterfly arrangement in which the energy (in units of J_{wb}) of a spin state denoted by $(S_t, S_{\text{Mn}}, S_{\text{Fe}})$ is plotted as a function of $J_{\text{bb}}/J_{\text{wb}}$. The correlation diagram clearly demonstrates the ground state variation as a function of the ratio of $J_{\text{bb}}/J_{\text{wb}}$, which is also consistent with the experimental findings for the different carboxylate bridging ligands within the heterometallic Fe_2Mn_2 core. As an example, the ground state $S_t = 3$ has component S_{Fe} and S_{Mn} values of 5 and 2, respectively. These values result from different relative orientations of $S_{\text{Fe}(3)}$, $S_{\text{Fe}(4)}$, $S_{\text{Mn}(1)}$, $S_{\text{Mn}(2)}$, which is represented below as an overall spin alignment due to spin frustration.

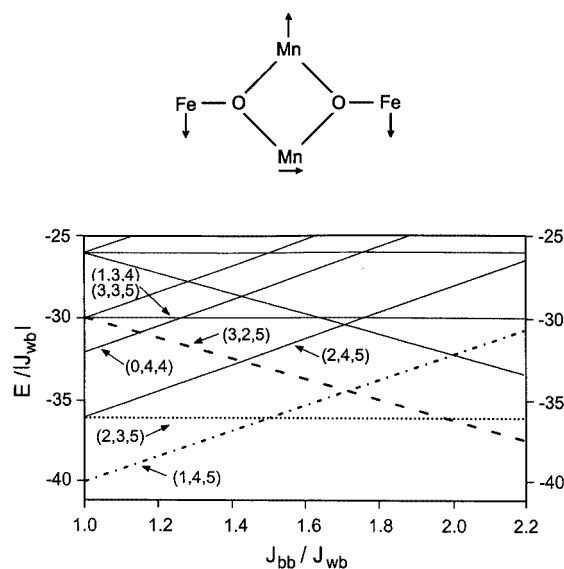


Figure 10. A selected energy-level diagram for the $[\text{Fe}_2\text{Mn}_2\text{O}_2]^{8+}$ core emphasising the ground state variation as a function of the ratio $J_{\text{bb}}/J_{\text{wb}}$; spin states are denoted by S_t , S_{Mn} and S_{Fe} , where $S_t = S_{\text{Mn}} + S_{\text{Fe}}$.

Concluding Remarks

The results described in the present paper show that not only homometal tetranuclear metal clusters of Fe^{III} and Mn^{III} with a butterfly disposition, $[\text{M}_4(\mu_3\text{-O})_2]^{8+}$, can be isolated, but also their mixed-metal analogues $[\text{Fe}_2^{\text{III}}\text{Mn}_2^{\text{III}}(\mu_3\text{-O})_2]^{8+}$ are easily accessible. The tetranuclear cores are amenable to carboxylate bridging ligand variation but the structural parameters show insignificant variation. Although the spin ground states resulting from the exchange interactions within the $[\text{Fe}_4\text{O}_2]^{8+}$ and $[\text{Mn}_4\text{O}_2]^{8+}$ cores are little affected by the peripheral carboxylate ligands, variation of the six carboxylates (acetate, benzoate, triphenyl acetate, benzoate, chloroacetate propionate) causes significant changes in the electronic ground state structure ($S_t = 1–3$) of the $[\text{Fe}_2\text{Mn}_2\text{O}_2]^{8+}$ core. As the crystallographic data exclude steric effects as the cause of the ground state variation, the electronic (donor) properties seem to be responsible for the dependence of spin ground states on the nature of the bridging carboxylates. Presum-

Table 9. Crystal data and structure refinement for **1**, **3**, **5**, **6** and **8**

	1	3	5	6	8
Empirical formula	C ₇₄ H ₈₅ ClFe ₄ N ₈ O ₁₉	C ₇₄ H ₈₅ ClMn ₄ N ₈ O ₁₉	C ₃₈ H ₆₁ ClFe ₂ Mn ₂ N ₈ O ₁₆	C ₇₄ H ₈₅ ClFe ₂ Mn ₂ N ₈ O ₁₉	C ₅₃ H ₆₇ ClFe ₂ Mn ₂ N ₈ O ₁₆ ·2CH ₃ CN
Formula mass	1649.35	1645.71	1142.98	1647.53	1411.28
Temperature [K]	293(2)	293(2)	100(2)	100(2)	100(2)
Crystal system	orthorhombic	orthorhombic	tetragonal	orthorhombic	monoclinic
Space group	<i>Pna</i> 2 ₁	<i>Pna</i> 2 ₁	<i>P4</i> (1)2(1)2	<i>Pna</i> 2 ₁	<i>P2</i> ₁ / <i>n</i>
Unit cell dimensions [Å]	<i>a</i> = 16.329(4) <i>b</i> = 18.644(4) <i>c</i> = 25.009(6) <i>α</i> = <i>β</i> = <i>γ</i> = 90°	<i>a</i> = 16.317(3) <i>b</i> = 18.655(4) <i>c</i> = 25.001(5) <i>α</i> = <i>β</i> = <i>γ</i> = 90°	<i>a</i> = 11.6230(9) <i>b</i> = 11.6230(9) <i>c</i> = 35.827(2) <i>α</i> = <i>β</i> = <i>γ</i> = 90°	<i>a</i> = 16.144(2) <i>b</i> = 18.396(2) <i>c</i> = 24.759(3) <i>α</i> = <i>β</i> = <i>γ</i> = 90°	<i>a</i> = 16.0785(6) <i>b</i> = 14.6897(5) <i>c</i> = 27.5133(10) <i>β</i> = 106.23°
Volume [Å ³]; <i>Z</i>	7613.7(3); 4	7610.1(3); 4	4840.0(6); 4	7353(2); 4	6239.3(4); 4
Density (calcd.) [Mg/m ³]	1.439	1.436	1.569	1.488	1.502
Absorpt. coeff. [mm ^{−1}]	0.857	0.759	1.227	0.836	0.969
<i>F</i> (000)	3432	3416	2368	3424	2928
Crystal size [mm]	0.40 × 0.37 × 0.12	0.50 × 0.45 × 0.07	0.31 × 0.28 × 0.12	0.42 × 0.24 × 0.09	0.30 × 0.25 × 0.25
Reflections collected	8991	9056	54594	59215	53728
Independent reflections	8991	8648	9541	20348	14147
Data/restraints/parameters	8972/214/931	8634/321/954	9536/0/316	20331/1/964	14124/0/801
Absolute structure parameter	0.00(3)	−0.01(3)	0.012(12)	−0.016(8)	—
Final <i>R</i> 1 [<i>I</i> > 2σ(<i>I</i>)]	0.0770	0.0827	0.0396	0.0439	0.0436
<i>R</i> 2 (all data)	0.178	0.168	0.0965	0.0961	0.1021

ably, spin coupling through carboxylate is not negligible, in contrast to the prevailing notion. Thus, future low molecular weight structural modelling of metalloproteins is expected to be guided by proper choice of the carboxylate ligands, in order to mimic the amino acids in the biomolecules.

The [M₄O₂]⁸⁺ tetranuclear cores are structurally incongruent with currently known biological metal sites and hence might be irrelevant from a biological view point. However, being readily prepared and amenable to carboxylate variation, **5**–**10** have proven useful starting points to increase our knowledge on fine-tuning the spin properties of molecular aggregates. This fine-tuning is a result of spin frustration. Both the lowest and the intermediate spin ground states have been observed in the isostructural complexes **5**–**10** which vary only in the nature of their carboxylate bridging ligands. As is seen from Figure 10 “spin-frustration degeneracy” of the ground state leading to unusual electronic properties is expected for the [Fe₂Mn₂O₂]⁸⁺ core if *J*_{bb}/*J*_{wb} ≈ 1.52 and 2.0.

Experimental Section

General: CAUTION: Although we experienced no difficulties, the unpredictable behaviour of perchlorate salts necessitates extreme caution in their handling. The complex LFeCl₃ was prepared as described previously.^[36] All other reagents were used as received. Elemental microanalyses were performed by the microanalytical laboratory Kolbe, Mülheim. Iron and manganese were determined spectrophotometrically by using pyridine-2,6-dicarboxylic acid as described in the literature.^[37] Perchlorate ion was determined gravimetrically as tetraphenylarsonium perchlorate. Infrared spectra were measured as KBr disks with a Perkin–Elmer FT-IR spectro-

meter 2000. The magnetochemical measurements of the powdered samples were performed with a Quantum Design SQUID-Magnetometer, MPMS generally in a field of 1 T. The samples were put in gelatine capsules and the response function was measured four times for each of 32 measured temperature points. Diamagnetic contributions were estimated for each compound by making use of Pascal's constants. The Mössbauer spectrometer worked in the conventional constant-acceleration mode with a ⁵⁷Co/Rh source. Isomer shifts are given relative to α-Fe at room temperature.

X-ray Crystallography: The crystallographic data for **1**, **3**, **5**, **6** and **8** are summarised in Table 9. Graphite-monochromated Mo-*K*_α radiation (λ = 0.71073 Å) was used throughout. X-ray diffraction data were collected with a Siemens R3m/V diffractometer for **1** and **3**. Dark brown single crystals of **5**, **6** and **8** were fixed with perfluoropolyether on glass fibres and mounted on a Siemens SMART diffractometer equipped with a cryogenic nitrogen cold stream, and intensity data were collected at 100(2) K. Final cell constants were obtained from a least-squares fit of the setting angles of several thousand strong reflections. Intensity data were corrected for Lorentz and polarisation effects. An empirical absorption correction by *Ψ* scans was applied for **1** and **3**; intensity data of **5** and **8** were corrected for absorption using the program SADABS (G. M. Sheldrick, University of Göttingen, 1994) giving maximum and minimum transmission factors of 0.928 and 0.736 for **5** and 0.853 and 0.768 for **8**. Intensities of **6** were left uncorrected. The Siemens ShelXTL, Vers. 5.0 (Siemens Industrial Automation, Inc., 1994) software package was used for solution, refinement and artwork of the structures. Neutral atom scattering factors of the program were used. All structures were solved and refined by direct methods and difference Fourier techniques. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were placed at calculated positions and refined as riding atoms with isotropic displacement parameters. A crystallographic twofold axis passes through the central acetate bridge of the complex cation of **5** and the perchlorate anion is disordered since this axis is not coincident with the twofold axis of the ClO₄[−] moiety. The disorder was satis-

factorily modelled by refining the complete anion slightly displaced from the axis with an occupation factor of 0.5. A phenyl group of a benzilate ligand in **6** was found to be disordered and therefore a split atom model was used. Two positions of the phenyl ring were refined with occupancies of 0.5 each. CCDC-187680 (**1**), -187681 (**3**), -187705 (**5**), -187706 (**6**) and -187707 (**8**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223/336-0333; E-mail: deposit@ccdc.cam.ac.uk].

Preparation of Complexes: Complexes **1** and **2** were prepared similarly by using a modified procedure for the corresponding acetate-bridged tetranuclear Fe^{III} compound.^[4]

$[\text{L}_2\text{Fe}^{\text{III}}_4(\text{salox})_2(\mu_3\text{-O})_2(\text{Ph}_2\text{C}(\text{OH})\text{COO})_3]\text{ClO}_4$ (1**):** All operations were carried out under argon. $\text{Fe}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.30 g, 1 mmol), sodium diphenylglycolate (benzilate) (0.50 g, 2 mmol) and salicylaldehyde (0.27 g, 2 mmol) were added to vigorously stirred, degassed methanol (60 mL). The resulting suspension was stirred at room temperature for 1 h to yield a dark violet solution. This solution was charged with a solid sample of $[\text{LFeCl}_3]^{[36]}$ (0.33 g, 1 mmol), sodium diphenylglycolate (benzilate) (0.75 g, 3 mmol) and triethylamine (1 mL). The suspension was refluxed for 1 h and then filtered to remove some dark solid, identified as $[\text{LFe}^{\text{III}}(\text{salox})_3\text{Fe}^{\text{III}}]$ by IR as described earlier.^[24b] Sodium perchlorate monohydrate (0.4 g) was added to the filtrate and the red-brown solution was kept in air at ambient temperature. After 1 d, the red-brown crystals were filtered off and air-dried. Yield: 390 mg (47%). $\text{C}_{74}\text{H}_{85}\text{ClFe}_4\text{N}_8\text{O}_{19}$ (1648.35): calcd. C 53.89, H 5.19, N 6.79, Fe 13.54, ClO_4 6.03; found C 53.9, H 5.1, N 6.8, Fe 13.7, ClO_4 5.8. MS (ESI positive in $\text{CH}_3\text{CN}/\text{H}_2\text{O}$): m/z (%) = 1549 (100) $[\text{M}]^+$. IR (KBr): $\tilde{\nu}$ = 3472, 1600, 1569, 1157, 700, 669, 648, 638 cm^{-1} .

$[\text{L}_2\text{Fe}^{\text{III}}_4(\text{salox})_2(\mu_3\text{-O})_2(\text{Ph}_3\text{CCOO})_3]\text{ClO}_4$ (2**):** Complex **2** was obtained similarly to complex **1** with sodium triphenylacetate used instead of sodium diphenylglycolate as the carboxylate source. Dark brown crystals were obtained. Yield: 410 mg (42%). $\text{C}_{92}\text{H}_{97}\text{ClFe}_4\text{N}_8\text{O}_{16}$ (1829.63): calcd. C 60.39, H 5.34, N 6.12, Fe 12.21, ClO_4 5.43; found C 58.4, H 5.4, N 6.0, Fe 12.3, ClO_4 5.5. MS (ESI positive in $\text{CH}_3\text{CN}/\text{H}_2\text{O}$): m/z (%) = 1730 (100) $[\text{M}]^+$. IR (KBr): $\tilde{\nu}$ = 1594, 1155, 1567, 699, 671, 652, 623 cm^{-1} .

$[\text{L}_2\text{Mn}^{\text{III}}_4(\text{salox})_2(\mu_3\text{-O})_2(\text{Ph}_2\text{C}(\text{OH})\text{COO})_3]\text{ClO}_4$ (3**):** Step 1: A suspension of diphenylglycolic acid (0.46 g, 2 mmol) and sodium hydroxide (0.08 g, 2 mmol) in water (30 mL) was stirred vigorously for 15 min. $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (0.20 g, 1 mmol) was added and stirring was continued for a further 15 min. The precipitated solid was filtered off, washed thoroughly with water, and dried for 24 h under vacuum. Step 2: A suspension of the dried solid obtained from step 1 and salicylaldehyde (0.27 g, 2 mmol) in methanol (40 mL) containing triethylamine (1 mL) was refluxed in air for 0.5 h to obtain a dark green suspension. The green suspension was charged with LMnCl_3 ^[38] (0.33 g, 1 mmol) under argon and treated with triethylamine (0.5 mL). The resulting suspension was refluxed under argon for 0.5 h and then filtered to remove some green solid (presumably $[\text{Mn}(\text{Hsalox})_3]$). Sodium perchlorate monohydrate (0.8 g) was added, and after 1–2 d the dark brown solution yielded deep brown crystals of **3**, which were collected by filtration and air-dried. Yield: 275 g (ca. 33%). $\text{C}_{74}\text{H}_{85}\text{ClMn}_4\text{N}_8\text{O}_{19}$ (1645.71): calcd. C 54.00, H 5.21, N 6.81, Mn 13.35, ClO_4 6.04; found C 53.8, H 5.1, N 6.8, Mn 13.1, ClO_4 5.9. IR (KBr): $\tilde{\nu}$ = 3472, 1617, 1592, 1574, 1158 cm^{-1} .

$[\text{L}_2\text{Mn}^{\text{III}}_4(\text{salox})_2(\mu_3\text{-O})_2(\text{Ph}_3\text{CCOO})_3]\text{ClO}_4$ (4**):** Complex **4** was prepared similarly to **3** with triphenylacetic acid as the carboxylate source. Deep brown crystals were obtained in moderately good yield (45%). $\text{C}_{92}\text{H}_{97}\text{ClMn}_4\text{N}_8\text{O}_{16}$ (1825.99): calcd. C 60.51, H 5.35, N 6.14, Mn 12.03, ClO_4 5.45; found C 58.9, H 5.5, N 6.2, Mn 12.2, ClO_4 5.1. MS (ESI positive in CH_3CN): m/z (%) = 1727 (80) $[\text{M}]^+$, 1484 (100) $[\text{M} - \text{L}(\text{Mn})(\text{O})]^+$, 1439 (60) $[\text{M} - (\text{C}_6\text{H}_5)_3\text{CCOO}]^+$. IR (KBr): $\tilde{\nu}$ = 3441, 1587, 1541, 1152 cm^{-1} . Complex **4** was also prepared using CH_3CN as solvent.

$[\text{L}_2\text{Fe}^{\text{III}}_2(\mu_3\text{-O})_2(\text{salox})_2(\mu\text{-OOC}\cdot\text{CH}_3)_3\text{Mn}^{\text{III}}_2]\text{ClO}_4$ (5**):** “Basic manganese(III) acetate”^[39] (0.27 g, 1 mmol) was added to a vigorously stirred solution of salicylaldehyde (0.135 g, 1 mmol) in methanol (60 mL). The resulting suspension was stirred at room temperature for 0.5 h to yield a dark brown solution which was then charged with a solid sample of LFeCl_3 (0.33 g, 1 mmol), sodium acetate (0.24 g, 3.0 mmol) and triethylamine (2 mL). The suspension was refluxed for 1 h and then filtered to remove some green solid (presumably $[\text{Mn}(\text{Hsalox})_3]$). Sodium perchlorate monohydrate (0.4 g) was added to the clear solution and the red-brown solution was kept at ambient temperature in a closed vessel. After 12 h, the dark brown crystals were filtered off and air-dried. Yield: 400 mg (70%). $\text{C}_{38}\text{H}_{61}\text{ClFe}_2\text{Mn}_2\text{N}_8\text{O}_{16}$ (1142.98): calcd. C 39.93, H 5.38, N 9.80, Fe 9.77, Mn 9.61, ClO_4 8.70; found C 39.7, H 5.4, N 9.8, Fe 9.9, Mn 9.5, ClO_4 8.9. IR (KBr): $\tilde{\nu}$ = 1594, 1544, 1155, 755, 743, 663 cm^{-1} .

$[\text{L}_2\text{Fe}^{\text{III}}_2(\mu_3\text{-O})_2(\text{salox})_2(\mu\text{-OOC}\cdot\text{C}(\text{OH})\text{Ph})_3\text{Mn}^{\text{III}}_2]\text{ClO}_4$ (6**):** A solution containing $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (0.20 g, 1 mmol), salicylaldehyde (0.27 g, 2 mmol) diphenylglycolic acid (0.63 g, 3 mmol) and triethylamine (1 mL) in methanol (60 mL) was heated to reflux for 0.5 h. LFeCl_3 (0.33 g, 1 mmol) and sodium diphenylglycolate (0.25 g, 1 mmol) were added to the resulting suspension. The mixture was refluxed for 1 h and then filtered to remove some green solid. The red-brown solution was kept at room temperature following addition of $\text{NaClO}_4 \cdot \text{H}_2\text{O}$ (0.8 g). After 24 h, the deep brown crystals were filtered off and air-dried. Yield: 510 mg (ca. 62%). $\text{C}_{74}\text{H}_{85}\text{ClFe}_2\text{Mn}_2\text{N}_8\text{O}_{19}$ (1647.53): calcd. C 53.95, H 5.20, N 6.80, Fe 6.78, Mn 6.67, ClO_4 6.04; found C 53.80, H 5.1, N 6.8, Fe 6.5, Mn 6.4, ClO_4 5.5. MS (ESI positive in CH_3CN): m/z (%) = 1547 (100), 1548 (90) $[\text{M}]^+$. IR (KBr): $\tilde{\nu}$ = 3742, 1617, 1592, 1540, 1158, 704, 670, 638, 603 cm^{-1} .

$[\text{L}_2\text{Fe}^{\text{III}}_2(\mu_3\text{-O})_2(\text{salox})_2(\mu\text{-OOC}\cdot\text{CPh}_3)_3\text{Mn}^{\text{III}}_2]\text{ClO}_4$ (7**), $[\text{L}_2\text{Fe}^{\text{III}}_2(\mu_3\text{-O})_2(\text{salox})_2(\mu\text{-OOC}\cdot\text{Ph})_3\text{Mn}^{\text{III}}_2]\text{ClO}_4$ (**8**), $[\text{L}_2\text{Fe}^{\text{III}}_2(\mu_3\text{-O})_2(\text{salox})_2(\mu\text{-OOCCH}_2\text{Cl})_3\text{Mn}^{\text{III}}_2]\text{ClO}_4$ (**9**), $[\text{L}_2\text{Fe}^{\text{III}}_2(\mu_3\text{-O})_2(\text{salox})_2(\mu\text{-OOC}\cdot\text{CH}_2\text{CH}_3)_3\text{Mn}^{\text{III}}_2]\text{ClO}_4$ (**10**):** Complexes **7–10** were prepared according to the same protocol for **6** using triphenylacetic acid (**7**), benzoic acid (**8**), chloroacetic acid (**9**) or propionic acid (**10**) as the bridging carboxylate sources. Red-brown crystals were obtained with yields in the range 40–50%.

7: $\text{C}_{52}\text{H}_{97}\text{ClFe}_2\text{Mn}_2\text{N}_8\text{O}_{16}$ (1827.81): calcd. C 60.45, H 5.35, N 6.13, Fe 6.11, ClO_4 5.44; found C 58.9, H 5.4, N 6.3, Fe 6.0, Mn 6.01, ClO_4 5.8. MS (ESI positive in $\text{CH}_3\text{CN}/\text{H}_2\text{O}$): m/z (%) = 1727 (100) $[\text{M}]^+$. IR (KBr): $\tilde{\nu}$ = 1591, 1540, 701, 670, 645, 612 cm^{-1} .

8: $\text{C}_{53}\text{H}_{67}\text{ClFe}_2\text{Mn}_2\text{N}_8\text{O}_{16}$ (1329.18): calcd. C 47.89, H 5.08, N 8.43, Fe 8.40, Mn 8.27, ClO_4 7.48; found C 48.1, H 5.0, N 8.5, Fe 8.4, Mn 8.2, ClO_4 7.9. IR (KBr): $\tilde{\nu}$ = 1594, 1541, 1157, 738, 723, 663, 636 cm^{-1} .

9: $\text{C}_{38}\text{H}_{58}\text{Cl}_4\text{Fe}_2\text{Mn}_2\text{N}_8\text{O}_{16}$ (1246.30): calcd. C 36.62, H 4.69, N 8.99, Fe 8.96, Mn 8.82, ClO_4 8.00; found C 35.0, H 5.0, N 9.0, Fe 9.2, Mn 8.8, ClO_4 8.1. IR (KBr): $\tilde{\nu}$ = 1594, 1543, 1156, 757, 745, 663 cm^{-1} .

10: $\text{C}_{41}\text{H}_{67}\text{ClFe}_2\text{Mn}_2\text{N}_3\text{O}_{16}$ (1185.06): calcd. C 41.55, H 5.70, N 9.46, Fe 9.43, Mn 9.27, ClO_4 8.39; found C 42.0, H 5.6, N 9.6, Fe 9.1, Mn 9.5, ClO_4 8.4. IR (KBr): $\tilde{\nu}$ = 1592, 1538, 1158, 704, 672, 640, 602 cm^{-1} .

Acknowledgments

This work was initiated in Bochum. Our thanks are due to Mrs. M. Hess, H. Schucht (Mülheim) and M. Winter (Bochum) for their technical assistance. Support from the Max Planck Society and Fonds der Chemischen Industrie is gratefully acknowledged.

- [1] V. I. Ponomarev, L. O. Atovmyan, S. A. Bobkova, K. I. Turté, *Dokl. Akad. Nauk. SSSR* **1984**, 274, 368.
- [2] W. H. Armstrong, M. E. Roth, S. J. Lippard, *J. Am. Chem. Soc.* **1987**, 109, 6318.
- [3] J. M. McCusker, J. B. Vincent, E. A. Schmitt, M. L. Mino, K. Shin, D. K. Coggin, P. M. Hagen, J. C. Huffman, G. Christou, D. N. Hendrickson, *J. Am. Chem. Soc.* **1991**, 113, 3012.
- [4] P. Chaudhuri, M. Winter, P. Fleischhauer, W. Haase, U. Flörke, H.-J. Haupt, *Inorg. Chim. Acta* **1993**, 212, 241.
- [5] L. Wu, M. Pressprich, P. Coppens, M. J. DeMarco, *Acta Crystallogr., Sect. C* **1993**, 49, 1255.
- [6] M. W. Wemple, D. K. Coggin, J. B. Vincent, J. K. McCusker, W. E. Streib, J. C. Huffman, D. N. Hendrickson, G. Christou, *J. Chem. Soc., Dalton Trans.* **1998**, 719.
- [7] [7a] K. Wieghardt, K. Pohl, I. Jibril, G. Huttner, *Angew. Chem. Int. Ed. Engl.* **1984**, 23, 77. [7b] C. Delfs, D. Gatteschi, L. Pardi, R. Sessoli, K. Wieghardt, D. Hanke, *Inorg. Chem.* **1993**, 32, 3099. [7c] A.-L. Barra, D. Gatteschi, R. Sessoli, *Chem. Eur. J.* **2000**, 6, 1608.
- [8] [8a] V. L. Pecoraro, Ed. *Manganese Redox Enzymes*, VCH Verlagsgesellschaft, Weinheim, **1992**. [8b] H. Sigel, A. Sigel, Ed. *Metal Ions in Biological Systems*, Marcel Dekker, New York, **2000**, vol. 37. [8c] R. H. Holm, E. I. Solomon (Guest Eds.), *Chem. Rev.* **1996**, no. 7.
- [9] J. B. Vincent, C. Christmas, H.-R. Chang, Q. Li, P. D. Boyd, J. C. Huffman, D. N. Hendrickson, G. Christou, *J. Am. Chem. Soc.* **1989**, 111, 2086.
- [10] E. Libby, J. K. McCusker, E. A. Schmitt, K. Folting, D. N. Hendrickson, G. Christou, *Inorg. Chem.* **1991**, 30, 3486.
- [11] E. Bouwman, M. A. Bolcar, E. Libby, J. C. Huffman, K. Folting, G. Christou, *Inorg. Chem.* **1992**, 31, 5185.
- [12] M. W. Wemple, H.-L. Tsai, S. Wang, J. B. Claude, W. E. Streib, J. C. Huffman, D. N. Hendrickson, G. Christou, *Inorg. Chem.* **1996**, 35, 6437.
- [13] P. Chaudhuri, M. Winter, P. Fleischhauer, W. Haase, U. Flörke, H.-J. Haupt, *J. Chem. Soc., Chem. Commun.* **1993**, 566.
- [14] P. Chaudhuri, F. Birkelbach, M. Winter, V. Staemmler, P. Fleischhauer, W. Haase, U. Flörke, H.-J. Haupt, *J. Chem. Soc., Dalton Trans.* **1994**, 2313.
- [15] O. Kahn, *Molecular Magnetism*, VCH Publishers, Weinheim, **1993**.
- [16] [16a] F. Birkelbach, U. Flörke, H.-J. Haupt, C. Butzlaff, A. X. Trautwein, K. Wieghardt, P. Chaudhuri, *Inorg. Chem.* **1998**, 37, 2000. [16b] F. Birkelbach, M. Winter, U. Flörke, H.-J. Haupt, C. Butzlaff, M. Lengen, E. Bill, A. X. Trautwein, K. Wieghardt, P. Chaudhuri, *Inorg. Chem.* **1994**, 33, 3990. [16c] C. Krebs, M. Winter, T. Weyhermüller, E. Bill, K. Wieghardt, P. Chaudhuri, *J. Chem. Soc., Chem. Commun.* **1995**, 1913. [16d] P. Chaudhuri, M. Winter, P. Fleischhauer, W. Haase, U. Flörke, H.-J. Haupt, *J. Chem. Soc., Chem. Commun.* **1990**, 1728. [16e] C. N. Verani, E. Rentschler, T. Weyhermüller, E. Bill, P. Chaudhuri, *J. Chem. Soc., Dalton Trans.* **2000**, 4263.
- [17] A few selected examples: [17a] K. E. Vostrikova, D. Luneau, W. Wernsdorfer, P. Rey, M. Verdagner, *J. Am. Chem. Soc.* **2000**, 122, 718. [17b] C. Diaz, J. Ribas, R. Costa, J. Tercero, M. S. E. Fallah, X. Solans, M. Forit-Bardia, *Eur. J. Inorg. Chem.* **2000**, 675. [17c] A. Aukauloo, X. Ottenwaelder, R. Ruiz, Y. Journaux, Y. Pei, E. Riviere, M. C. Munoz, *Eur. J. Inorg. Chem.* **2000**, 951. [17d] B. Cervera, R. Ruiz, F. Lloret, M. Julve, J. Faus, C. M. Munoz, Y. Journaux, *Inorg. Chim. Acta* **1999**, 288, 57. [17e] E. Colacio, J. M. Dominguez-Vera, M. Ghazi, R. Kivekäs, M. Klinga, J. M. Moreno, *Inorg. Chem.* **1998**, 37, 3040. [17f] S. Mohanta, K. K. Nand, L. K. Thompson, U. Flörke, K. Nag, *Inorg. Chem.* **1998**, 37, 1465.
- [18] [18a] O. Kahn, *Adv. Inorg. Chem.* **1995**, 43, 179. [18b] K. S. Murray, *Adv. Inorg. Chem.* **1995**, 43, 261.
- [19] [19a] P. D. W. Boyd, Q. Li, J. B. Vincent, K. Folting, H. R. Chang, W. E. Streib, J. C. Huffman, G. Christou, D. N. Hendrickson, *J. Am. Chem. Soc.* **1988**, 110, 8537. [19b] D. Sessoli, H. L. Tsai, A. R. Schake, S. Wang, J. B. Vincent, K. Folting, D. Gatteschi, G. Christou, D. N. Hendrickson, *J. Am. Chem. Soc.* **1993**, 115, 1804. [19c] D. Gatteschi, A. Caneschi, L. Pardi, R. Sessoli, *Science* **1994**, 265, 1054. [19d] S. M. J. Aubin, M. W. Wemple, D. M. Adams, H. L. Tsai, G. Christou, D. N. Hendrickson, *J. Am. Chem. Soc.* **1996**, 118, 7746. [19e] A. L. Barra, A. Caneschi, A. Cornia, D. Fabrizi de Biani, D. Gatteschi, C. Sangregorio, R. Sessoli, L. Sorace, *J. Am. Chem. Soc.* **1999**, 121, 5302. [19f] G. Aromi, S. M. J. Aubin, M. A. Bolcar, G. Christou, H. J. Eppley, K. Folting, D. N. Hendrickson, J. C. Huffman, R. C. Squire, H.-L. Tsai, S. Wang, M. W. Wemple, *Polyhedron* **1998**, 17, 3005 and references therein. [19g] J. Larinova, M. Gross, M. Pilkington, H. Andres, H. Stoeckli-Evans, H. U. Güdel, S. Decurtins, *Angew. Chem. Int. Ed.* **2000**, 1605. [19h] D. Gatteschi, R. Sessoli, A. Cornia, *Chem. Commun.* **2000**, 725 and references therein.
- [20] D. N. Hendrickson, *Research Frontiers in Magnetochemistry* (Ed.: C. J. O'Connor), World Scientific Singapore, **1993**, p. 87.
- [21] O. Kahn, *Chem. Phys. Lett.* **1997**, 265, 109.
- [22] F. Ephraïm, *Ber. Dtsch. Chem. Ges.* **1930**, 63, 1928.
- [23] [23a] E. Toyota, K. Umakoshi, Y. Yamamoto, *Bull. Chem. Soc. Jpn.* **1995**, 68, 858. [23b] J. M. Thorpe, R. L. Beddoes, D. Collison, C. D. Garner, M. Helliwell, J. M. Holmes, P. A. Tasker, *Angew. Chem. Int. Ed.* **1999**, 38, 1119. [23c] S. J. Rettig, A. Storr, J. Trotter, *Acta Crystallogr., Sect. C* **1992**, 48, 1587. [23d] K. R. Manolov, *Russ. J. Inorg. Chem.* **1967**, 12, 1431.
- [24] [24a] P. Chaudhuri, *Proc. Indian Acad. Sci. (Chem. Sci.)* **1999**, 111, 397. [24b] C. N. Verani, E. Bothe, D. Burdinski, T. Weyhermüller, U. Flörke, P. Chaudhuri, *Eur. J. Inorg. Chem.* **2001**, 2161.
- [25] E. Bill, C. Krebs, M. Winter, M. Gerdan, A. X. Trautwein, U. Flörke, H.-J. Haupt, P. Chaudhuri, *Chem. Eur. J.* **1997**, 3, 193.
- [26] P. Chaudhuri, M. Hess, T. Weyhermüller, E. Bill, H.-J. Haupt, U. Flörke, *Inorg. Chem. Commun.* **1998**, 1, 39.
- [27] P. Chaudhuri, M. Hess, E. Rentschler, T. Weyhermüller, U. Flörke, *New J. Chem.* **1998**, 533.
- [28] P. Chaudhuri, M. Winter, B. P. C. Della Védova, P. Fleischhauer, W. Haase, U. Flörke, H.-J. Haupt, *Inorg. Chem.* **1991**, 30, 4777.
- [29] R. D. Cannon, R. P. White, *Progr. Inorg. Chem.* **1988**, 36, 195.
- [30] [30a] P. Gülich, in *Mössbauer Spectroscopy* (Ed.: U. Gonser), Springer-Verlag, Berlin, Heidelberg, New York, **1975**. [30b] N. N. Greenwood, T. C. Gibb, *Mössbauer Spectroscopy*, Chapman and Hall, London, **1971**.
- [31] G. J. Long, W. T. Robinson, W. P. Tappmeyer, D. L. Bridges, *J. Chem. Soc., Dalton Trans.* **1973**, 573.
- [32] [32a] J. H. Rodriguez, H. Ok, Y.-M. Xia, P. G. Debrunner, B. E. Hinrichs, T. Meyer, N. H. Packard, *J. Phys. Chem.* **1996**, 100, 6849. [32b] J. H. Rodriguez, Y.-M. Xia, P. G. Debrunner, P. Chaudhuri, K. Wieghardt, *J. Am. Chem. Soc.* **1996**, 118, 7542.
- [33] A. Bino, R. Chayat, E. Pedersen, A. Schneider, *Inorg. Chem.* **1991**, 30, 856.
- [34] S. L. Castro, Z. Sun, C. M. Grant, J. C. Bollinger, D. N. Hendrickson, G. Christou, *J. Am. Chem. Soc.* **1988**, 120, 2365.
- [35] C. Canada-Vilalta, J. C. Huffman, G. Christou, *Polyhedron* **2001**, 20, 1785.

- [36] P. Chaudhuri, M. Winter, K. Wieghardt, S. Gehring, W. Haase, B. Nuber, J. Weiss, *Inorg. Chem.* **1988**, 27, 1564.
- [37] H. Hartkamp, *Z. Anal. Chem.* **1964**, 199, 183.
- [38] K. Wieghardt, U. Bossek, B. Nuber, J. Weiss, J. Bonvoisin, M. Corbella, S. E. Vitols, J. J. Girerd, *J. Am. Chem. Soc.* **1988**, 110, 7398.
- [39] F. A. Cotton, G. Wilkinson, *Advanced Inorganic Chemistry*, 5th ed., John Wiley & Sons, New York, **1988**, p. 704.

Received July 3, 2002
[I02363]