

Self-Assembly of Dimeric Mn^{III}–Schiff-Base Complexes Tuned by Perchlorate Anions

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Keywords: Manganese / Self-assembly / Anions / Schiff bases / Peroxidase

The synthesis and structural and spectroscopic characterisation of 12 manganese(III)–Schiff-base complexes of the formula $[\text{MnL}^n(\text{H}_2\text{O}/\text{CH}_3\text{OH})_2](\text{ClO}_4)(m\text{H}_2\text{O})$ ($m = 0, 1$) are described. The multidentate H_2L^n and H_4L^n Schiff-base ligands were obtained by condensation of different diamines (1,2-diaminoethane, 1,2-diamino-2-methylethane, 1,2-diamino-2,2-dimethylethane, 1,3-diamino-2,2-dimethylpropane) and 2,3-dihydroxybenzaldehyde, 3-methoxy-2-hydroxybenzaldehyde or 3-ethoxy-2-hydroxybenzaldehyde. The crystal structures of H_2L^3 and H_4L^{10} ligands were solved by X-ray crystallography, revealing their ability to bind metal centres. Recrystallisation of complexes **2** and **8** from methanol yielded single crystals of $[\text{MnL}^2(\text{H}_2\text{O})_2](\text{ClO}_4)$ and $[\text{MnL}^8(\text{H}_2\text{O})_2](\text{ClO}_4)$. Their X-ray characterisation shows a tetragonally elongated octahedral geometry for the manganese coordination sphere, formed by the chelation of the N_2O_2 donor set of

the inner compartment of the Schiff base to the equatorial plane of the octahedron and by the binding of two water molecules in the axial positions. The octahedron entities are linked in pairs by μ -aquo bridges between neighbouring axial water molecules and also by π – π stacking interactions, establishing dimeric structures. Perchlorate anions are accommodated in the cavities of the framework and form hydrogen bonds with the aqua ligands, leading to infinite spirals of the complexes generated by a screw axis along a . Moreover, the peroxidase activity of the crystallographically solved complexes **2** and **8**, studied in the presence of the water-soluble trap ABTS, agrees with the predicted rate according to the activity/rhombicity correlation.

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Introduction

Crystal engineering of supramolecular architectures sustained by noncovalent intermolecular forces represents a rapidly expanding field that offers potential for the development of new types of functional solids.^[1,2] The self-assembly of metal-organic frameworks is highly influenced by factors such as the geometric requirements of metal ions,^[3,4] the ligand design,^[5,6] the solvents used for crystallisation^[7] or the selection of the counteranions.^[8] Understanding the role of these factors may extend our knowledge of the relevant structural types and establishes proper synthetic strategies that lead to the desired species with predictable structures and properties.

In recent times one of our research goals constitutes the study of supramolecular chemistry of manganese(III).^[9–11] The coordination chemistry of this species has been extensively studied^[12,13] due to its rich redox behaviour, where manganese(III) complexes are the active sites of numerous

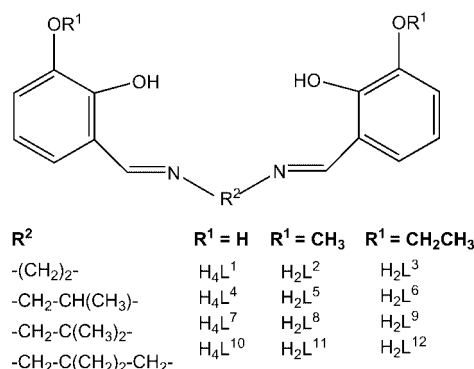
enzymes,^[14] but studies focusing on their multidimensional arrangements are less abundant. This paper presents new results from our intention of studying in depth the multidimensional arrangements of manganese(III) chemistry.

We have already shown how the introduction of chloride anions may induce the self-assembly of Mn^{III} complexes, through a hydrogen-bonding net, to give 2D supramolecular architectures^[10] when the ligand has hydroxy functional groups in adequate positions. We are now exploring the use of weakly coordinating anions such as perchlorates, nitrates, etc., to construct Mn^{III} polymer networks.^[15–18] The ability of these anions for establishing hydrogen bonds would allow new supramolecular architectures to be obtained and would also lead to systems of interest for the selective recognition between anions and receptors.^[19,20]

Herein we report a series of Mn^{III}–Schiff-base complexes associated by perchlorate counteranions, using ligands with adequate OH groups. The selected Schiff-base ligands, H_4L^n and H_2L^n (see Scheme 1), contain six and four potential donor atoms, respectively. They have in common an inner compartment with two imine nitrogen atoms and two phenol oxygen atoms, but H_4L^n ligands have an extra couple of outer phenol groups, while H_2L^n ligands present two outer methoxy or ethoxy groups.

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Scheme 1.

Results and Discussion

Synthesis and Spectroscopic Studies

The Schiff-base ligands were obtained in almost quantitative yield by the well-known experimental procedure, and afterwards they were characterised by elemental analysis, electrospray, IR, ¹H- and ¹³C NMR spectroscopy, as well as the measurements of their melting points. Additionally, H₂L³ and H₄L¹⁰ gave crystals suitable for their characterisation by X-ray crystallography.

The manganese complexes were prepared following a variation of the Boucher method reported by us previously.^[21] The manganese compounds obtained by this synthetic route, in high yield, are sparingly soluble in water and common organic solvents, but are quite soluble in MeOH, DMF and DMSO. Elemental analyses establish their general formula as [MnL^m(H₂O/CH₃OH)₂](ClO₄)(mH₂O) (*m* = 0, 1).

All these complexes show similar IR spectral features (Table 1), exhibiting a strong band between 1621–1610 cm⁻¹ attributable to ν(C=N_{imine}), which is shifted 7–22 cm⁻¹ lower than that in the free ligand. An up-frequency shift of the ν(CO_{phenol}) band to higher frequency (6–21 cm⁻¹) is also observed. These data suggest the coordination of the Schiff base in its dianionic form to the metal through the inner phenol oxygen and the imine nitrogen atoms.

The IR spectra also show broad unsplit bands ca. 1100 cm⁻¹, together with bands at 630 cm⁻¹, indicative of the presence of the uncoordinated perchlorate anion.

The presence of a broad band at about 3400 cm⁻¹ is associated with coordinated and/or solvated water/methanol molecules, but unfortunately it interferes with the observation of uncoordinated hydroxy groups.^[22]

The ES mass spectra exhibit peaks relating to fragments [MnL]⁺, which thus further corroborate coordination of the ligand to the manganese ion. The appearance of minor peaks in some complexes that could be assigned to the [Mn₂L₂]⁺ dimeric entity (see Table 1) suggests their tendency to dimerise, although this spectroscopic technique is not sensitive enough to unambiguously detect either these dimers or the coordinated water molecules in every case.

The room temperature magnetic moments of the complexes are listed in Table 1. They exhibit values close to the spin-only value of 4.9 BM, as expected for a high-spin magnetically diluted d⁴ manganese(III) ion, indicating little or no antiferromagnetic interaction.

The electronic spectroscopic data recorded are very similar for all compounds 1–12, indicating that the Mn^{III} complexes are behaving as high-spin octahedral d⁴ systems, probably suffering a significant Jahn–Teller distortion which affects the spectra and complicates its interpretation. The characteristic UV broad band obtained at 480–490 nm (ϵ = 2600–3300 L mol⁻¹ cm⁻¹) corresponds to the ⁵E_g ← ⁵T_{2g} transition, and the peak appearing around 300 nm (ϵ = 21000–23000 L mol⁻¹ cm⁻¹) can be attributed to the Schiff-base ligand → Mn^{III} LMCT band.

Furthermore, the conductivity measurements in DMF give Λ_M values of 90–60 μS cm⁻¹, indicating a behaviour attributable to 1:1 electrolytes.^[23]

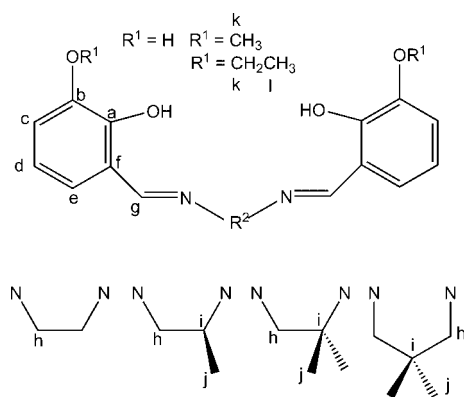
Paramagnetic ¹H NMR spectroscopic studies of these Mn^{III} complexes were undertaken using [D₆]dmsO as the solvent. The data are presented in Table 1. The interpretation of the data was based on previous findings for manganese(III) complexes with related Schiff-base ligands.^[9,24] The spectra contain proton resonances that lie outside the diamagnetic region (δ = 0–14 ppm) due to the well-known isotropically shifting of the ligand protons for high-spin Mn^{III} complexes in an octahedral field. In this sense, the

Table 1. Magnetic moments, conductivity measurements, IR, ¹H NMR and mass spectrometric data of the complexes.

	ES [amu] ^[a]	IR [cm ⁻¹]				μ [BM]	Λ [μS cm ⁻¹]	¹ H NMR [ppm]	
		ν(O–H)	ν(C=N) ^[b]	N(C–O) ^[b]	ν(Cl–O)			H4	H5
[Mn(H ₂ L ¹)(H ₂ O) ₂](ClO ₄)(H ₂ O) (1)	353 (705)	3421	1621 (1633)	1254 (1246)	1087; 636	4.9	75	–34.05	–20.10
[Mn(L ²)(H ₂ O) ₂](ClO ₄)(H ₂ O) (2)	382	3419	1621 (1633)	1255 (1249)	1087; 636	4.9	66	–27.37	–19.20
[Mn(L ³)(H ₂ O) ₂](ClO ₄)(H ₂ O) (3)	410 (819)	3457	1621 (1629)	1258 (1250)	1109; 623	5.0	70	–27.72	–19.16
[Mn(H ₂ L ⁴)(H ₂ O)(CH ₃ OH)](ClO ₄) (4)	368	3424	1619 (1626)	1257 (1236)	1087; 636	5.0	75	–34.15	–21.99
[Mn(L ⁵)(H ₂ O) ₂](ClO ₄)(H ₂ O) (5)	396 (791)	3417	1619 (1627)	1256 (1250)	1084; 636	5.0	60	–27.60	–18.93
[Mn(L ⁶)(H ₂ O) ₂](ClO ₄)(H ₂ O) (6)	424	3418	1619 (1631)	1259 (1249)	1109; 624	5.0	88	–27.64	–18.82
[Mn(H ₂ L ⁷)(H ₂ O)(CH ₃ OH)](ClO ₄) (7)	382	3420	1610 (1624)	1258 (1241)	1086; 625	5.0	75	–32.61	–20.08
[Mn(L ⁸)(H ₂ O) ₂](ClO ₄) (8)	409 (817)	3413	1610 (1629)	1255 (1249)	1085; 625	5.0	62	–27.80	–18.64
[Mn(L ⁹)(H ₂ O) ₂](ClO ₄) (9)	438 (875)	3421	1612 (1628)	1254 (1248)	1120; 625	5.0	88	–28.01	–18.96
[Mn(H ₂ L ¹⁰)(H ₂ O)(CH ₃ OH)](ClO ₄) (10)	395	3416	1620 (1639)	1253 (1240)	1120; 620	5.0	62	–30.27	–20.08
[Mn(L ¹¹)(H ₂ O) ₂](ClO ₄)(H ₂ O) (11)	424 (846)	3418	1610 (1632)	1254 (1247)	1108; 624	4.9	63	–20.10	–14.50
[Mn(L ¹²)(H ₂ O) ₂](ClO ₄) (12)	451	3429	1612 (1633)	1256 (1250)	1120; 625	4.9	89	–20.72	–16.75

[a] Peaks corresponding to [MnL]⁺, and, in parentheses, to [Mn₂L₂]⁺. [b] Bands corresponding to the free ligands in parentheses.

data obtained from these NMR spectroscopic studies serve to corroborate the formation of the manganese(III) complexes since two sets of upfield sharp peaks corresponding to the H4 and H5 protons of the aromatic rings (Scheme 2) are observed. Clearly the upfield signals (ranging from –20.10 to –34.15 ppm) arise from H4 protons, while the downfield resonances (–14.50 to –21.99 ppm) arise from H5 protons. Our experience shows that signals in *ortho* positions to donor atoms are not observable for these kinds of complexes by paramagnetic ¹H NMR spectroscopy. Since H4 signals are discernible for all complexes, including **1**, **4**, **7** and **10**, with external hydroxy groups in the aromatic rings of the Schiff bases, the NMR spectra suggest no coordination through these groups to the metal ion.

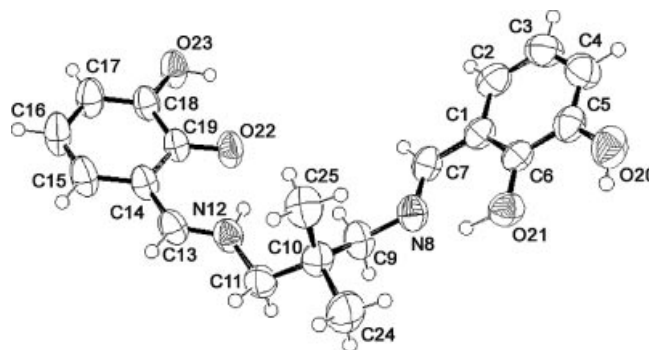


Scheme 2.

Crystallographic Studies of Ligands H₂L³ and H₄L¹⁰

Crystals of H₄L¹⁰ suitable for X-ray studies were obtained by slow evaporation of a methanol solution of the ligand. The crystal structure, with the numbering scheme, is shown in Figure 1. Selected bond lengths and angles are given in Table 2.

The crystal structure is made up of H₄L¹⁰ discrete molecules. The C7–N8 and N12–C13 distances of 1.276(2) and 1.290(2) Å, respectively, are consistent with N=C double bonding. One of the four oxygen atoms, O22, lacks a hydrogen atom, appearing in the carbonyl form, which is corroborated by the C19–O22 distance of 1.2928(18) Å, in accordance with a C=O double bond. The other three oxygen

Figure 1. Molecular structure of H₄L¹⁰ showing the atomic numbering scheme.

atoms form phenol groups, and they present longer C–O distances [C5–O20 1.365(2) Å, C6–O21 1.347(2) Å, C18–O23 1.361(2) Å], corresponding to the expected single bonds.

The study of these distances reveals the transfer of one proton from a hydroxy group of each molecule to the neighbouring nitrogen atom N12. This process is favoured by the so-called “proton-sponge” effect,^[25] which consists of the increase in the basicity of the imine nitrogen atoms due to the spatial nearness of their lone pairs. The instability of a situation of proximity of these two lone pairs is then solved by the attraction of one phenol hydrogen atom by one of the nitrogen atoms. This leads to the formation of a relatively strong [N–H···O]⁺ intramolecular bond [H22···O22 1.75(2) Å, N12···O22 2.5914(19) Å and N12–H22···O22 145.2°]. Despite the symmetry of the compound, a second proton transfer to the other imine nitrogen atom does not occur since it would mean a very unfavourable situation, involving the formation of two neighbouring [N–H]⁺ groups and preventing the [N–H···O]⁺ intramolecular hydrogen bond.

An additional intramolecular hydrogen bond exists between the N8 imine nitrogen atom and the neighbouring phenol oxygen atom [H21···N8 1.55(3) Å, O21···N8 2.5767(19) Å and O21–H21···N8 146.2°]. These intramolecular hydrogen bonds are typical of Schiff bases derived from salicylaldehydes.^[26] Besides, intermolecular interactions by hydrogen bonds can also be observed between the phenol oxygen atoms of neighbouring molecules.

Table 2. Selected bond lengths [Å] and angles [°] for the ligands H₂L³ and H₄L¹⁰.

H ₂ L ³				H ₄ L ¹⁰			
C10–N11	1.272(5)	N11–C12	1.461(5)	C7–N8	1.276(2)	N8–C9	1.461(2)
C1–O13	1.344(4)	C6–O7	1.372(5)	N12–C13	1.290(2)	C11–N12	1.459(2)
O7–C8	1.417(5)			C5–O20	1.365(2)	C6–O21	1.347(2)
				C18–O23	1.361(2)	C19–O22	1.2928(18)
N11–C10–C2	121.9(4)	C10–N11–C12	120.2(4)	N8–C7–C1	121.93(15)	C7–N8–C9	119.28(15)
C12B–C12–N11	110.5(5)	O13–C1–C2	121.8(4)	N8–C9–C10	111.63(14)	N12–C11–C10	112.87(14)
O13–C1–C6	118.5(4)	C5–C6–O7	126.6(4)	C13–N12–C11	124.97(15)	N12–C13–C14	123.76(15)
O7–C6–C1	113.9(4)	C6–O7–C8	117.4(4)	O20–C5–C4	120.35(18)	O20–C5–C6	119.23(17)
O7–C8–C9	106.2(4)			O21–C6–C5	118.15(15)	O21–C6–C1	122.08(15)
				O22–C19–C14	122.78(14)	O22–C19–C18	120.28(14)
				O23–C18–C17	119.47(16)	O23–C18–C19	119.44(14)

According to this crystal structure study, the rather planar conformation of the set N8–N12–O21–O22 suggests that this ligand should easily act as tetradentate donor in the equatorial plane about an octahedral metal centre. However, we cannot predict the role of the outer phenol oxygen atoms of each aldehyde residue during complexation as they could coordinate, for instance, to the metal centre by an axial position, but also their role could be limited to intermolecular hydrogen-bond interactions.

Slow evaporation of a methanol solution of ligand H_2L^3 gives crystals, suitable for X-ray diffraction studies, of $\text{C}_{20}\text{H}_{24}\text{N}_2\text{O}_4$. The crystal structure is displayed in Figure 2 with the atom numbering scheme adopted. Selected bond lengths and angles are in Table 2.

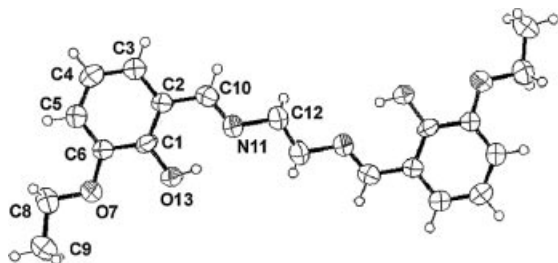


Figure 2. Molecular structure of H_2L^3 showing the atomic numbering scheme.

The crystal structure reveals that H_2L^3 exists as discrete molecules, and it is composed of two identical 3-methoxy-2-hydroxybenzylidene moieties connected by the flexible C12–C12B methylene chain (so-called spacer in supramolecular chemistry), so we will only discuss one of them. The C10–N11 distance of 1.272(5) Å is consistent with C=N double bonding. Both imine groups are fully localised in the molecule. The angle of 120.2(4)° around the N11 atom confirms its sp^2 character.

The disposition adopted by the free ligand in the solid state is conditioned by two strong intramolecular hydrogen-bond interactions which form two six-membered rings. These interactions arise from the contact between the hydroxy and the imine groups. In this case and contrary to the situation described for H_4L^{10} , both hydroxy oxygen atoms retain their hydrogen atoms. As expected, the O13–H13...N11 [H13...N11 1.59(7) Å, O13...N11 2.555(5) Å and O13–H13...N11 154(6)°] hydrogen bonding establishes an almost planar N11–C10–C2–C1–O13–H13 ring.

This kind of Schiff-base ligand, with a flexible spacer, produces this type of “open” structure as we have previously found in similar ligands.^[27,28] These and other similar ligands present adequate conditions to be useful in the synthesis of octahedral complexes, occupying the equatorial positions around the metal centre.

Crystallographic Studies of Complexes 2 and 8

Recrystallisation of $[\text{MnL}^2(\text{H}_2\text{O})_2](\text{ClO}_4)$ (**2**) and $[\text{MnL}^8(\text{H}_2\text{O})_2](\text{ClO}_4)$ (**8**) from methanol solutions by slow evaporation afforded brown crystals from which we deter-

mined their molecular structures. Both crystal structures show similar features; thereby, they will be discussed together. An ORTEP view of **8** with the atomic numbering scheme is shown in Figure 3. Experimental details are given in Table 5. Main bond lengths and angles are listed in Table 3.

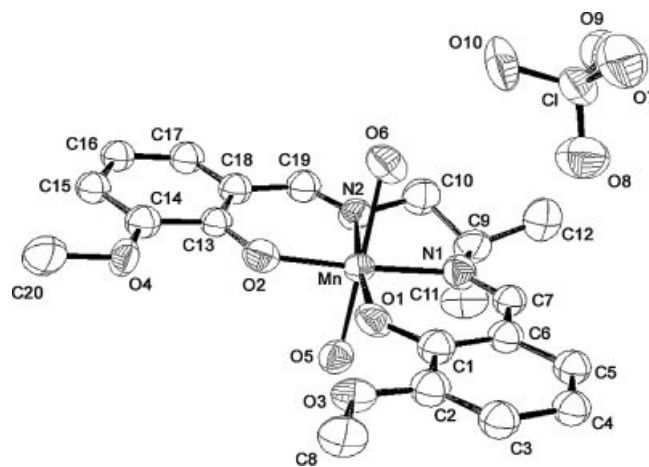


Figure 3. Molecular structure of **8** showing the atomic numbering scheme.

Table 3. Selected bond lengths [Å] and angles [°] for complexes **2** and **8**.

Complex 2			
Mn1–O13a	1.864(3)	Mn1–N4	1.968(4)
Mn1–O43a	1.866(3)	Mn1–O1W	2.265(4)
Mn1–N1	1.961(4)	Mn1–O2W	2.314(4)
Mn...Mn	4.8886(4)		
O13a–Mn1–O43a	92.61(13)	O13a–Mn1–N1	92.11(15)
O43a–Mn1–N1	175.26(16)	O13a–Mn1–N4	174.84(15)
O43a–Mn1–N4	91.93(15)	N1–Mn1–N4	83.36(17)
O13a–Mn1–O1W	93.84(13)	O43a–Mn1–O1W	92.15(13)
N1–Mn1–O1W	87.17(14)	N4–Mn1–O1W	88.43(14)
O13a–Mn1–O2W	88.20(15)	O43a–Mn1–O2W	87.93(17)
N1–Mn1–O2W	92.58(19)	N4–Mn1–O2W	89.52(17)
O1W–Mn1–O2W	177.95(15)		
Complex 8			
Mn–O1	1.8482(15)	Mn–N2	1.9582(18)
Mn–O2	1.8529(16)	Mn–O5	2.2366(17)
Mn–N1	1.9648(19)	Mn–O6	2.3607(19)
Mn...Mn	4.8896(4)		
O1–Mn–O2	93.21(7)	O1–Mn–N2	174.10(7)
O2–Mn–N2	92.07(7)	O1–Mn–N1	92.83(7)
O2–Mn–N1	173.80(7)	N2–Mn–N1	81.83(8)
O1–Mn–O5	89.04(6)	O2–Mn–O5	90.35(7)
N2–Mn–O5	93.55(7)	N1–Mn–O5	91.17(7)
O1–Mn–O6	93.81(6)	O2–Mn–O6	90.49(7)
N2–Mn–O6	83.51(7)	N1–Mn–O6	87.70(7)
O5–Mn–O6	176.97(6)		

The crystallographic analyses show $[\text{MnL}^n(\text{H}_2\text{O})_2]^+$ mononuclear cationic complexes, where the geometry around each manganese(III) ion can be described as distorted octahedral. The structure of these cations comprises the planar Schiff-base ligand tightly bound to the manganese(III) ion through the inner N_2O_2 compartment by the N_{imine} and O_{phenol} atoms (Mn– N_{imine} bond lengths of 1.95–1.97 Å and

Mn–O_{phenol} of 1.84–1.87 Å are typical of such complexes and corroborate the bisdeprotonation of the ligands),^[9,10,29] occupying the equatorial positions and giving rise to two six-membered chelate rings (which are nearly planar) and an additional five-membered chelate ring. The coordination sphere around each manganese centre is then completed by capping water molecules. The axial Mn–O distances (ranging from 2.23 to 2.36 Å) are considerably longer than the equatorial Mn–O bond lengths quoted earlier, indicating that the Jahn–Teller elongation expected for a high-spin d⁴ manganese(III) ion is present among these complexes. The deviation from an ideal octahedral geometry is also revealed by the range of angles observed around the metal centre (from 81.83° to 93.84°), as well as by the interaxial angle OW–Mn–OW of 177.95° for **2** and 176.97° for **8**.

From the viewpoint of supramolecular chemistry, complexes **2** and **8** exhibit a topology constructed by hydrogen bonds, which help to stabilise the packing and induce the assembly of the mononuclear cationic complexes.

The superstructure of the complexes involves associations through a combination of π -aryl interactions and hydrogen bonds between capping water and outer phenoxy and axial water oxygen atoms of the neighbouring Schiff-base ligand. This results in Mn $\cdots$ Mn distances of about 4.90 Å, which are short for monomeric compounds; these types of [MnL(H₂O)₂]₂²⁺ systems have been reported by us previously^[30,31] as μ -aquo dimers (Figure 4). However, these Mn $\cdots$ Mn distances are too long to establish intermetallic interactions between neighbouring manganese ions, in accordance with the non-antiferromagnetic behaviour shown by the magnetic studies.



Figure 4. Ball-and-stick diagram of the μ -aquo dimer formed for **2** through hydrogen bonds.

Moreover, the μ -aquo dimers are interconnected by hydrogen bonding involving the perchlorate counterions. In this way, pairs of neighbouring μ -aquo dimers are linked by two perchlorate anions. The hydrogen-bonding interactions involving perchlorate anions with their symmetry codes for compounds **2** and **8** are given in Table 4. This hydrogen-bonding scheme arises from the interactions of two perchlorate

rate ions which establish two pairs of hydrogen bonds to two adjacent μ -aquo dimers. Each pair is directed from the perchlorate anions to the external capping water molecule of each dimeric building unit (see Figure 5). These multiple intermolecular interactions are extended into the solid to form infinite spirals generated by a screw axis along *a*. The 1D network of manganese dimers generates a kind of tunnel along the *c* axis. Perchlorate anions are accommodated in such cavities of the framework.

Table 4. Hydrogen-bonding scheme (distances and angles) involving perchlorate counterions for complexes **2** and **8**.

D–H $\cdots$ A [Å]	D–H [Å]	H $\cdots$ A [Å]	D $\cdots$ A [Å]	D–H $\cdots$ A [°]
Complex 2				
O2W–H12W $\cdots$ O2 ^[a]	0.80(7)	2.47(8)	3.10(2)	137(7)
O2W–H22W $\cdots$ O2	0.74(7)	2.01(7)	2.71(2)	157(7)
Complex 8				
O6–H61–O10	1.024(16)	1.981(19)	2.886(2)	146.(2)
O6–H62–O9 ^[b]	1.074(15)	2.178(15)	2.998(3)	131.3(15)

[a] Symmetry operations: 2 – *x*, 1 – *y*, 1 – *z*. [b] Symmetry operations: 1 – *x*, 1 – *y*, 1 – *z*.

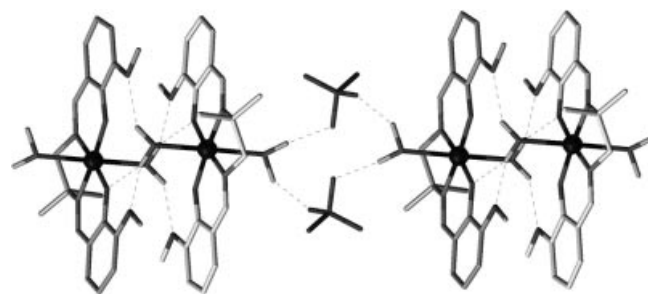


Figure 5. Stick diagram for **8** showing the hydrogen bonding between adjacent [MnL(H₂O)₂]₂²⁺ dimeric units through perchlorate anions.

A comparison between the role of perchlorate and chloride counterions as multiple hydrogen-bond acceptors for similar manganese(III) complexes derived from H₄L Schiff bases may be established. We have previously reported how each chloride ion could be involved in four O–H $\cdots$ Cl bonds, connecting three neighbouring cationic complexes and assembling them to constitute a 2D network.^[10] In the present work, we find each perchlorate anion is only able to form two hydrogen bonds. This behaviour implies preference is given to one direction and provokes a decrease in the dimensionality of the network.

Redox Properties and Peroxidase Essays

The electrochemical behaviour of some of the complexes (**2**, **3**, **5**, **7**, **8** and **12**) was studied by cyclic voltammetry. In all cases this technique exhibits a one-electron reduction-oxidation peak system in the 0 to –0.1 V potential range. The difference between the anodic and cathodic potentials indicates a redox reversible character. Moreover, these negative potentials belong to the range which would favour the

catalytic activity, as we have previously reported for other Mn^{III} -Schiff-base systems.^[31,32]

The peroxidase-like activity of the cited complexes was followed by the oxidation of the diammonium salt of 2,2'-azinobis(3-ethylbenzothiazoline)-6-sulfonic acid (ABTS) at pH 6.8. The reaction of ABTS with H_2O_2 in the presence of the complexes generates $\text{ABTS}^{+\cdot}$, which can be clearly identified by its characteristic absorption bands (415, 650, 735 and 815 nm) and measured quantitatively at $\lambda = 650$ nm since $\epsilon = 12000 \text{ M}^{-1} \text{ cm}^{-1}$ has been determined. The rate of formation of $\text{ABTS}^{+\cdot}$ ranges from 30–40% with respect to the initial ABTS. This shows an important capacity of hydrogen peroxide decomposition by the studied complexes. The activity is comparable to that of a previous series of Mn-Schiff-base complexes, reported by us, incorporating carboxylate ligands,^[31] but is much higher than an earlier Mn-Schiff-base series with the chloride counterion.^[10] Recently, we have tried to establish a correlation between peroxidase activity and the structural motifs of the complexes.^[31] We have postulated what seems to be an easy approach to predict the capacity of H_2O_2 decomposition by these types of complexes as a function of the tetragonal elongation of the octahedral geometry in the crystal structure. An axial water molecule in this class of distorted geometries constitutes a quite labile ligand, which would generate a vacant position in the coordination sphere to accommodate the substrate molecule.

In order to quantify the tetragonal elongation we have employed the "rhombicity" of the structure as the ratio between their manganese-axial-oxygen distances and their manganese-equatorial-oxygen distances. This correlation is also valid for the data taken for complexes **2** and **8** of this work. Their Mn-Ow/Mn-Oeq ratios of 1.24 and 1.27, respectively, are compatible with their peroxidase activity.

Conclusions

We can conclude that these types of manganese(III) complexes, formed from Schiff bases with inner and outer O-X (X = H, CH_3 , CH_2CH_3) groups, constitute suitable building units for establishing rich hydrogen-bonding networks. In the present work, the selection of the proper spacer in the Schiff-base ligand allows formation of $[\text{MnL}]_2^{2+}$ dimeric units, which can be connected through perchlorate counterions to form 1D chains. The lower dimensionality of the network with respect to the case of a chloride counterion ($2\text{D} \rightarrow 1\text{D}$) can be interpreted in terms of the lower symmetry of the perchlorate (tetrahedral) than that of the chloride (spherical), involving a higher directionality of the network. The ability of these types of complexes to accommodate different anions in the vacancies of the framework becomes an interesting research field for selective recognition between anions and receptors, beyond their worthwhile redox behaviour.

Experimental Section

Physical Measurements: Elemental analyses were performed with a Carlo Erba model 1108 CHNS-O elemental analyser. The IR spec-

tra were recorded as KBr discs with a Bruker IFS-66V FTIR spectrophotometer and UV-Vis spectra with a Varian Cary IE. ^1H - and ^{13}C NMR spectra were recorded with a Bruker WH 300 MHz spectrometer using DMSO as the solvent and SiMe_4 as an internal reference. ES mass spectra were recorded with a Hewlett-Packard LC-MSD Series 1100a spectrometer. Conductivities of 10^{-3} M solutions in DMF were measured with a Crison Micro CM 2200 conductimeter. Room-temperature magnetic susceptibilities were measured using a Faraday balance MSB-MKI by Evans; $\text{HgCo}(\text{NCS})_4$ was employed as a susceptibility standard.

Electrochemical measurements were performed with an EG&G PAR model 273 potentiostat, controlled by EG&G PAR model 270 software. A Metrohm model 6.1204.000 graphite disc coupled to a Metrohm model 628-10 rotating electrolyte device was used as a working electrode. A saturated calomel electrode was used as a reference, and a platinum wire was used as an auxiliary electrode. All measurements were made with ca. $10^{-3} \text{ mol dm}^{-3}$ solutions of the complexes in dimethylformamide using $0.2 \text{ mol dm}^{-3} \text{ NBu}_4\text{PF}_6$ as a supporting electrolyte. Cyclic voltammetry measurements were performed with a static graphite electrode.

Materials: 2,3-Dihydroxybenzaldehyde (Sigma-Aldrich), 3-methoxy-2-hydroxybenzaldehyde (Fluka Chemika), 3-ethoxy-2-hydroxybenzaldehyde (Fluka Chemika), diamines [1,2-diaminoethane, 1,2-diamino-2-methylethane, 1,2-diamino-2,2-dimethylethane, 1,3-diamino-2,2-dimethylpropane] (Aldrich) and manganese(II) perchlorate hexahydrate (Fluka) were used as received without further purification.

Preparation of the Ligands: The hexadentate Schiff bases, H_xL^n , used in this study were prepared by condensation of the appropriate diamine with 2,3-dihydroxybenzaldehyde, 3-methoxy-2-hydroxybenzaldehyde or 3-ethoxy-2-hydroxybenzaldehyde in methanol.^[33,34] They were isolated in virtually quantitative yield and satisfactorily characterised by elemental analysis, ^1H - and ^{13}C NMR spectroscopy, ES mass spectroscopy and IR spectroscopy. This can be typified by the following preparation of H_4L^1 .

H_4L^1 : To a methanol solution (120 mL) of 2,3-dihydroxybenzaldehyde (4.00 g, 28.96 mmol) was added 1,2-diaminoethane (0.97 mL, 14.48 mmol). This mixture was heated at reflux in a round-bottomed flask fitted with a Dean Stark trap to remove the water produced during the reaction. After heating for 3 h, the solution was concentrated to yield a yellow solid. The product was collected by filtration, washed with diethyl ether and dried in air. $\text{C}_{16}\text{H}_{16}\text{N}_2\text{O}_4$ (300.30): calcd. C 63.9, H 5.4, N 9.3; found C 63.3, H 5.6, N 9.4. ^1H NMR (300 MHz, $[\text{D}_6]\text{DMSO}$): $\delta = 8.54$ (s, 2 H), 6.65–6.85 (m, 6 H), 3.93 (s, 4 H) ppm. ^{13}C NMR (75 MHz, $[\text{D}_6]\text{DMSO}$): $\delta = 167.1$ (C_g), 151.0 (C_a), 145.8 (C_b), 118.1 (C_f), 58.0 (C_h) ppm. ES-MS: $m/z = 301.2$. IR: $\tilde{\nu} = \nu(\text{O-H})$ 3258, $\nu(\text{C=N})$ 1633, $\nu(\text{C-O})$ 1246 cm^{-1} . M.p. 240 °C.

H_2L^2 : 3-Methoxy-2-hydroxybenzaldehyde (2.00 g, 13.15 mmol) and 1,2-diaminoethane (0.41 mL, 6.57 mmol). $\text{C}_{18}\text{H}_{20}\text{N}_2\text{O}_4$ (328.37): calcd. C 65.8, H 6.2, N 8.5; found C 65.7, H 6.2, N 8.6. ^1H NMR (300 MHz, $[\text{D}_6]\text{DMSO}$): $\delta = 13.42$ (br.), 8.56 (s, 2 H), 6.79–7.01 (t, d, d, 6 H), 3.92 (s, 4 H), 3.76 (s, 6 H) ppm. ^{13}C NMR (75 MHz, $[\text{D}_6]\text{DMSO}$): $\delta = 167.7$ (C_g), 152.3 (C_a), 148.7 (C_b), 59.0 (C_h), 56.5 (C_k) ppm. ES-MS: $m/z = 329.3$. IR: $\tilde{\nu} = \nu(\text{O-H})$ 3087, $\nu(\text{C=N})$ 1633, $\nu(\text{C-O})$ 1249 cm^{-1} . M.p. 165 °C.

H_2L^3 : 3-Ethoxy-2-hydroxybenzaldehyde (2.00 g, 12.04 mmol) and 1,2-diaminoethane (0.40 mL, 6.02 mmol). $\text{C}_{20}\text{H}_{24}\text{N}_2\text{O}_4$ (356.42): calcd. C 67.4, H 6.7, N 7.9; found C 66.9, H 6.8, N 7.1. ^1H NMR (300 MHz, $[\text{D}_6]\text{DMSO}$): $\delta = 8.54$ (s, 2 H), 6.72–6.99 (d, t, d, 6 H), 4.00 (q, 4 H), 3.97 (s, 4 H), 1.31 (t, 6 H) ppm. ^{13}C NMR (75 MHz,

[D₆]DMSO): δ = 167.7 (C_g), 152.5 (C_a), 147.8 (C_b), 64.7 (C_k), 59.1 (C_h), 15.4 (C_i) ppm. ES-MS: m/z = 357.4. IR: $\tilde{\nu}$ = $\nu(\text{O–H})$ 3467, $\nu(\text{C=N})$ 1629, $\nu(\text{C–O})$ 1250 cm^{−1}. M.p. 146 °C.

H₄L⁴: 2,3-Dihydroxybenzaldehyde (4.00 g, 28.96 mmol) and 1,2-diamino-2-methylethane (1.23 mL, 14.48 mmol). C₁₇H₁₈N₂O₄ (314.34): calcd. C 64.9, H 5.8, N 8.9; found C 64.8, H 5.8, N 8.7. ¹H NMR (300 MHz, [D₆]DMSO): δ = 13.53 (br.), 9.00 (br.), 8.55 (s, 1 H), 8.52 (s, 1 H), 6.62–6.86 (m, 6 H), 3.81 (d, 2 H), 1.33 (d, 3 H), 3.75–3.89 (m, 1 H) ppm. ¹³C NMR (75 MHz, [D₆]DMSO): δ = 167.1/165.3 (C_g), 151.2/150.5 (C_a), 145.1/145.7 (C_b), 118.0/118.2 (C_f), 63.6 (C_h), 63.1 (C_i), 19.9 (C_j) ppm. ES-MS: m/z = 315. IR: $\tilde{\nu}$ = $\nu(\text{O–H})$ 3240, $\nu(\text{C=N})$ 1626, $\nu(\text{C–O})$ 1236 cm^{−1}. M.p. 164 °C.

H₂L⁵: 3-Methoxy-2-hydroxybenzaldehyde (2.00 g, 13.15 mmol) and 1,2-diamino-2-methylethane (0.56 mL, 6.57 mmol). C₁₉H₂₂N₂O₄ (342.39): calcd. C 66.6, H 6.5, N 8.2; found C 66.5, H 6.8, N 8.2. ¹H NMR (300 MHz, [D₆]DMSO): δ = 13.50 (br.), 8.54 (s, 1 H), 8.51 (s, 1 H), 6.73–7.01 (m, 6 H), 3.82 (m, 1 H), 3.80 (d, 2 H), 1.31 (s, 6 H) ppm. ¹³C NMR (75 MHz, [D₆]DMSO): δ = 165.8/167.7 (C_g), 151.3 (C_a), 147.5 (C_b), 64.8 (C_h), 56.4/56.5 (C_k), 64.0 (C_i), 20.5 (C_j) ppm. ES-MS: m/z = 343.1. IR: $\tilde{\nu}$ = $\nu(\text{O–H})$ 3440, $\nu(\text{C=N})$ 1627, $\nu(\text{C–O})$ 1250 cm^{−1}. M.p. 137 °C.

H₂L⁶: 3-Ethoxy-2-hydroxybenzaldehyde (2.00 g, 12.04 mmol) and 1,2-diamino-2-methylethane (0.51 mL, 6.02 mmol). C₂₁H₂₇N₂O₄ (371.45): calcd. C 67.9, H 7.3, N 7.5; found C 67.3, H 7.2, N 7.5. ¹H NMR (300 MHz, [D₆]DMSO): δ = 13.5 (br.), 8.53 (s, 1 H), 8.50 (s, 1 H), 6.71–6.98 (d, d, t, 6 H), 4.00 (q, 4 H), 3.96 (s, 2 H), 3.75 (m, 1 H), 1.31 (d, 3 H), 1.29 (t, 6 H) ppm. ¹³C NMR (75 MHz, [D₆]DMSO): δ = 165.8/167.8 (C_g), 152.4 (C_a), 147.7 (C_b), 64.9 (C_k), 64.0 (C_i), 64.1 (C_h), 20.6 (C_j), 15.4 (C_i) ppm. ES-MS: m/z = 371.4. IR: $\tilde{\nu}$ = $\nu(\text{O–H})$ 3523, $\nu(\text{C=N})$ 1631, $\nu(\text{C–O})$ 1249 cm^{−1}. M.p. 91 °C.

H₄L⁷: 2,3-Dihydroxybenzaldehyde (4.00 g, 28.96 mmol) and 1,2-diamino-2,2-dimethylethane (1.52 mL, 14.48 mmol). C₁₈H₂₀N₂O₄ (328.37): calcd. C 65.8, H 6.1, N 8.5; found C 65.8, H 6.3, N 8.5. ¹H NMR (300 MHz, [D₆]DMSO): δ = 13.61/14.17 (br.), 8.95 (br.), 8.56 (s, 1 H), 8.52 (s, 1 H), 6.60–6.92 (m, 6 H), 3.79 (s, 2 H), 1.38 (s, 6 H) ppm. ¹³C NMR (75 MHz, [D₆]DMSO): δ = 167.4/162.8 (C_g), 152.2/150.9 (C_a), 145.9/145.7 (C_b), 118.1 (C_f), 68.2 (C_h), 59.4 (C_i), 25.0 (C_j) ppm. ES-MS: m/z = 329. IR: $\tilde{\nu}$ = $\nu(\text{O–H})$ 3227, $\nu(\text{C=N})$ 1645–1624, $\nu(\text{C–O})$ 1241 cm^{−1}. M.p. 183 °C.

H₂L⁸: 3-Methoxy-2-hydroxybenzaldehyde (2.00 g, 13.15 mmol) and 1,2-diamino-2,2-dimethylethane (0.69 mL, 6.57 mmol). C₂₀H₂₄N₂O₄ (356.42): calcd. C 67.6, H 6.9, N 7.8; found C 67.5, H 6.9, N 7.8. ¹H NMR (300 MHz, [D₆]DMSO): δ = 13.57 (br.), 8.54 (s, 1 H), 8.51 (s, 1 H), 6.72–7.04 (m, 6 H), 3.77 (s, 2 H), 3.74 (s, 6 H), 1.34 (s, 6 H) ppm. ¹³C NMR (75 MHz, [D₆]DMSO): δ = 163.4/167.9 (C_g), 152.9 (C_a), 148.7 (C_b), 69.4 (C_i), 60.4 (C_h), 56.3/56.4 (C_k), 25.7 (C_j) ppm. ES-MS: m/z = 357.0. IR: $\tilde{\nu}$ = $\nu(\text{O–H})$ 3333, $\nu(\text{C=N})$ 1629, $\nu(\text{C–O})$ 1249 cm^{−1}. M.p. 183 °C.

H₂L⁹: 3-Ethoxy-2-hydroxybenzaldehyde (2.00 g, 12.04 mmol) and 1,2-diamino-2,2-dimethylethane (0.63 mL, 6.02 mmol). C₂₂H₂₈N₂O₄ (384.47): calcd. C 68.7, H 7.3, N 7.3; found C 67.9, H 7.6, N 7.5. ¹H NMR (300 MHz, [D₆]DMSO): δ = 8.53 (s, 1 H), 8.50 (s, 1 H), 6.69–7.00 (d, d, t, 6 H), 4.00 (q, 4 H), 3.96 (s, 2 H), 1.34 (s, 6 H), 1.30 (t, 6 H) ppm. ¹³C NMR (75 MHz, [D₆]DMSO): δ = 167.9/168.0 (C_g), 152.4 (C_a), 147.8 (C_b), 69.4 (C_i), 64.7/64.8 (C_k), 60.3 (C_h), 25.7 (C_j), 15.4 (C_i) ppm. ES-MS: m/z = 385.4. IR: $\tilde{\nu}$ = $\nu(\text{O–H})$ 3433, $\nu(\text{C=N})$ 1628, $\nu(\text{C–O})$ 1248 cm^{−1}. M.p. 88 °C.

H₄L¹⁰: 2,3-Dihydroxybenzaldehyde (2.00 g, 14.48 mmol) and 1,3-diamino-2,2-dimethylpropane (0.86 mL, 7.24 mmol). C₁₉H₂₂N₂O₄ (342.39): calcd. C 66.7, H 6.5, N 8.2; found C 66.9, H 6.6, N 8.1. ¹H NMR (300 MHz, [D₆]DMSO): δ = 13.89 (br.), 9.02 (br.), 8.52

(s, 2 H), 6.68–6.88 (t, d, d, 6 H), 3.51 (s, 4 H), 1.01 (s, 6 H) ppm. ¹³C NMR (75 MHz, [D₆]DMSO): δ = 166.0 (C_g), 151.3 (C_a), 145.9 (C_b), 118.0 (C_f), 65.9 (C_k), 35.7 (C_i), 23.4 (C_j) ppm. ES-MS: m/z = 343. IR: $\tilde{\nu}$ = $\nu(\text{O–H})$ 3215, $\nu(\text{C=N})$ 1639, $\nu(\text{C–O})$ 1240 cm^{−1}. M.p. 180 °C.

H₂L¹¹: 3-Methoxy-2-hydroxybenzaldehyde (2.00 g, 13.15 mmol) and 1,3-diamino-2,2-dimethylpropane (0.78 mL, 6.57 mmol). C₂₁H₂₆N₂O₄ (370.45): calcd. C 68.1, H 7.0, N 7.6; found C 67.7, H 7.2, N 7.4. ¹H NMR (300 MHz, [D₆]DMSO): δ = 8.51 (s, 2 H), 6.76–7.03 (t, d, d, 6 H), 3.77 (s, 6 H), 3.47 (s, 4 H), 0.98 (s, 6 H) ppm. ¹³C NMR (75 MHz, [D₆]DMSO): δ = 167.3 (C_g), 152.6 (C_a), 148.8 (C_b), 124.0 (C_f), 67.4 (C_h), 56.6 (C_k), 24.3 (C_i, C_j) ppm. ES-MS: m/z = 371.4. IR: $\tilde{\nu}$ = $\nu(\text{O–H})$ 3439, $\nu(\text{C=N})$ 1632, $\nu(\text{C–O})$ 1247 cm^{−1}. M.p. 82 °C.

H₂L¹²: 3-Ethoxy-2-hydroxybenzaldehyde (2.00 g, 12.04 mmol) and 1,3-diamino-2,2-dimethylpropane (0.72 mL, 6.02 mmol). C₂₃H₃₀N₂O₄ (398.50): calcd. C 69.3, H 7.5, N 7.0; found C 68.7, H 7.6, N 6.9. ¹H NMR (300 MHz, [D₆]DMSO): δ = 13.85 (br.), 8.51 (s, 2 H), 6.74–7.02 (d, d, t, 6 H), 4.03 (q, 4 H), 3.48 (br.), 1.31 (t, 6 H), 0.98 (s, 6 H) ppm. ¹³C NMR (75 MHz, [D₆]DMSO): δ = 167.5 (C_g), 152.7 (C_a), 147.9 (C_b), 118.4 (C_f), 67.3 (C_h), 64.7 (C_k), 36.4 (C_i), 24.3 (C_j), 15.5 (C_i) ppm. ES-MS: m/z = 398.7. IR: $\tilde{\nu}$ = $\nu(\text{O–H})$ 3428, $\nu(\text{C=N})$ 1633, $\nu(\text{C–O})$ 1250 cm^{−1}. M.p. 64 °C.

Preparation of the Complexes: All the complexes were synthesised by air oxidation of the solution made up from Mn(ClO₄)₂·6H₂O and the Schiff base.^[21] A typical preparation of these complexes is outlined.

[Mn(H₂L⁴)(H₂O)(CH₃OH)](ClO₄) (4): H₄L⁴ (0.30 g, 0.95 mmol) was dissolved in methanol (40 mL), and then a solution of NaOH (1.90 mmol, 4 m) in methanol (0.48 mL) was added. After stirring for 10 min, a solution of Mn(ClO₄)₂·6H₂O (0.35 g, 0.95 mmol) in methanol (10 mL) was added, and the solution turned brown. (**Caution:** Although no problems were encountered in this work, perchlorates are potentially explosive and should be handled in only small quantities and with care!) The progress of the reaction was followed by TLC for 3 d, and the mixture was then filtered. The complex was obtained from the filtrate as a brown solid after crystallisation. It was isolated by filtration and washed with diethyl ether and dried in air. Yield: 0.37 g (75%). C₁₈H₂₂ClMnN₂O₁₀ (516.77): calcd. C 41.8, H 4.3, N 5.4; found C 42.0, H 4.1, N 5.6.

[Mn(H₂L¹)(H₂O)₂](ClO₄)(H₂O) (1): H₄L¹ (0.50 g, 1.66 mmol), Mn(ClO₄)₂·6H₂O (0.60 g, 1.66 mmol) and NaOH (0.83 mL, 3.32 mmol). Yield: 0.76 g (90%). C₁₆H₂₀ClMnN₂O₁₁ (506.73): calcd. C 37.9, H 4.0, N 5.5; found C 38.0, H 3.9, N 5.8.

[Mn(L²)(H₂O)₂](ClO₄)(H₂O) (2): H₂L² (0.33 g, 1.00 mmol), Mn(ClO₄)₂·6H₂O (0.36 g, 1.00 mmol) and NaOH (0.50 mL, 2.00 mmol). Yield: 0.35 g (65%). C₁₈H₂₄ClMnN₂O₁₁ (534.78): calcd. C 40.4, H 4.5, N 5.2; found C 40.1, H 4.3, N 5.2. Complex 2 was recrystallised from methanol solution, affording brown crystals adequate for X-ray diffraction studies.

[Mn(L³)(H₂O)₂](ClO₄)(H₂O) (3): H₂L³ (0.20 g, 0.56 mmol), Mn(ClO₄)₂·6H₂O (0.20 g, 0.56 mmol) and NaOH (0.28 mL, 1.12 mmol). Yield: 0.10 g (32%). C₂₀H₂₈ClMnN₂O₁₁ (562.84): calcd. C 42.7, H 5.0, N 5.0; found C 42.0, H 4.9, N 4.8.

[Mn(L⁵)(H₂O)₂](ClO₄)(H₂O) (5): H₂L⁵ (0.39 g, 1.00 mmol), Mn(ClO₄)₂·6H₂O (0.36 g, 1.00 mmol) and NaOH (0.50 mL, 2.00 mmol). Yield: 0.35 g (65%). C₁₉H₂₆ClMnN₂O₁₁ (548.81): calcd. C 41.6, H 4.8, N 5.1; found C 41.4, H 4.6, N 5.1.

[Mn(L⁶)(H₂O)₂](ClO₄)(H₂O) (6): H₂L⁶ (0.20 g, 0.54 mmol), Mn(ClO₄)₂·6H₂O (0.19 g, 0.54 mmol) and NaOH (0.27 mL,

Table 5. Crystal data and structure refinement for H_2L^3 , H_4L^{10} , **2** and **8**.

	H_2L^3	H_4L^{10}	2	8
Empirical formula	$\text{C}_{20}\text{H}_{24}\text{N}_2\text{O}_4$	$\text{C}_{19}\text{H}_{22}\text{N}_2\text{O}_4$	$\text{C}_{18}\text{H}_{22}\text{ClMnN}_2\text{O}_{10}$	$\text{C}_{20}\text{H}_{26}\text{ClMnN}_2\text{O}_{10}$
Formula weight	356.41	342.39	516.77	544.82
Temperature [K]	293(2)	293(2)	293(2)	293(2)
Wavelength [Å]	1.54180	0.71069	0.71073	0.71073
Crystal system	monoclinic	monoclinic	orthorhombic	monoclinic
Space group	$C2/c$	$P2_1/c$	$Pbca$	$P2_1/c$
a [Å]	22.581(5)	6.7030(4)	13.990(5)	13.4577(19)
b [Å]	7.0115(9)	13.8580(6)	13.349(5)	13.4504(17)
c [Å]	12.4645(19)	19.1350(10)	22.745(5)	14.375(2)
α [°]	90.00	90.00	90.000(5)	90.00
β [°]	108.336(15)	91.687(4)	90.000(5)	116.975(19)
γ [°]	90.00	90.00	90.000(5)	90.00
Volume [Å ³]	1873.3(6)	1776.68(16)	4248(2)	2319.0(6)
Z	4	4	8	4
D_c [g cm ⁻³]	1.264	1.280	1.616	1.560
Absorption coefficient [mm ⁻¹]	0.721	0.090	0.807	0.743
$F(000)$	760	728	2128	1128
Crystal size [mm]	$0.40 \times 0.10 \times 0.04$	$0.36 \times 0.28 \times 0.24$	$0.19 \times 0.18 \times 0.03$	$0.45 \times 0.40 \times 0.10$
Theta range for data collection [°]	4.12 to 65.26	1.81 to 26.33	1.79 to 21.99	1.70 to 24.97
Reflections collected	1694	3934	25121	4235
Independent reflections	1606 [$R(\text{int}) = 0.0922$]	3618 [$R(\text{int}) = 0.0134$]	2602 [$R(\text{int}) = 0.0876$]	4072 [$R(\text{int}) = 0.0160$]
Data/restraints/parameters	1606/0/124	3618/0/253	2602/356/337	4072/0/253
Goodness-of-fit on F^2	0.891	1.032	1.054	1.005
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0599$ $wR_2 = 0.1353$	$R_1 = 0.0456$ $wR_2 = 0.1371$	$R_1 = 0.0444$ $wR_2 = 0.1023$	$R_1 = 0.0260$ $wR_2 = 0.0539$
R indices (all data)	$R_1 = 0.1993$ $wR_2 = 0.1899$	$R_1 = 0.0605$ $wR_2 = 0.1477$	$R_1 = 0.0793$ $wR_2 = 0.1146$	$R_1 = 0.0392$ $wR_2 = 0.0642$

1.08 mmol). Yield: 0.21 g (68%). $\text{C}_{21}\text{H}_{31}\text{ClMnN}_2\text{O}_{11}$ (577.87): calcd. C 43.7, H 5.2, N 4.9; found C 44.0, H 5.0, N 4.7.

[Mn(H₂L⁷)(H₂O)(CH₃OH)](ClO₄) (7): H_4L^7 (0.30 g, 0.91 mmol), $\text{Mn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.33 g, 0.91 mmol) and NaOH (0.46 mL, 1.82 mmol). Yield: 0.29 g (60%). $\text{C}_{19}\text{H}_{24}\text{ClMnN}_2\text{O}_{10}$ (530.79): calcd. C 43.0, H 4.6, N 5.3; found C 42.7, H 4.3, N 5.3.

[Mn(L⁸)(H₂O)₂](ClO₄) (8): H_2L^8 (0.36 g, 1.00 mmol), $\text{Mn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.36 g, 1.00 mmol) and NaOH (0.50 mL, 2.00 mmol). Yield: 0.35 g (65%). $\text{C}_{20}\text{H}_{26}\text{ClMnN}_2\text{O}_{10}$ (544.82): calcd. C 44.1, H 4.8, N 5.1; found C 43.8, H 4.7, N 5.0. Single brown crystals, useful for X-ray diffraction studies, were obtained from slow evaporation of a methanol solution of complex **8**.

[Mn(L⁹)(H₂O)₂](ClO₄) (9): H_2L^9 (0.20 g, 0.52 mmol), $\text{Mn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.18 g, 0.52 mmol) and NaOH (0.26 mL, 1.04 mmol). Yield: 0.25 g (83%). $\text{C}_{22}\text{H}_{30}\text{ClMnN}_2\text{O}_{10}$ (572.87): calcd. C 46.1, H 5.2, N 4.9; found C 46.4, H 5.1, N 4.6.

[Mn(H₂L¹⁰)(H₂O)(CH₃OH)](ClO₄) (10): H_4L^{10} (0.30 g, 0.88 mmol), $\text{Mn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.32 g, 0.88 mmol) and NaOH (0.44 mL, 1.76 mmol). Yield: 0.34 g (70%). $\text{C}_{19}\text{H}_{26}\text{ClMnN}_2\text{O}_{10}$ (532.81): calcd. C 44.1, H 4.8, N 5.1; found C 44.3, H 4.6, N 5.0.

[Mn(L¹¹)(H₂O)₂](ClO₄)(H₂O) (11): H_2L^{11} (0.20 g, 0.68 mmol), $\text{Mn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.20 g, 0.68 mmol) and NaOH (0.34 mL, 1.35 mmol). Yield: 0.10 g (30%). $\text{C}_{21}\text{H}_{30}\text{ClMnN}_2\text{O}_{11}$ (576.86): calcd. C 43.7, H 5.2, N 4.9; found C 43.3, H 5.0, N 4.7.

[Mn(L¹²)(H₂O)₂](ClO₄) (12): H_2L^{12} (0.20 g, 0.50 mmol), $\text{Mn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.18 g, 0.50 mmol) and NaOH (0.25 mL, 1.00 mmol). Yield: 0.22 g (75%). $\text{C}_{23}\text{H}_{32}\text{ClMnN}_2\text{O}_{10}$ (586.90): calcd. C 47.1, H 5.5, N 4.8; found C 48.0, H 5.4, N 4.6.

Peroxidase Probes: Oxidation of 2,2'-azinobis(3-ethylbenzothiazoline-6-sulfonic acid) (ABTS) with H_2O_2 in the presence of the complexes was tested. An aqueous solution of ABTS (50 μL , 0.009 M, 4.5×10^{-7} mol) and a methanol solution of the complex

(10 μL , 10^{-3} M, 10^{-8} mol) were added to water (3 mL). The oxidation of ABTS started immediately after addition of an aqueous solution of H_2O_2 (50 μL , 10 M, 5×10^{-4} mol).

X-ray Crystallographic Studies: Crystals of H_2L^3 , H_4L^{10} , **2** and **8** suitable for X-ray diffraction studies were obtained by slow evaporation of methanol solutions of the cited solids. Data for H_4L^{10} and **2** were collected with a Smart CCD-1000 Bruker diffractometer employing graphite-monochromated Mo- K_α ($\lambda = 0.71073$ Å) radiation. Data for **8** were collected with a Nonius FR591-kappa CCD2000 diffractometer using graphite-monochromated Mo- K_α ($\lambda = 0.71073$ Å) radiation. Data for H_2L^3 were collected with a Nonius Mach3 diffractometer employing graphite-monochromated Cu- K_α ($\lambda = 1.54180$ Å) radiation. The structures were solved by direct methods^[35] and finally refined by full-matrix least-squares based on F^2 . An empirical absorption correction was applied using SADABS.^[36] All non-hydrogen atoms were anisotropically refined, and all hydrogen atoms were included in the model at geometrically calculated positions. Detailed data collection and refinement of the compounds are summarised in Table 5. CCDC-636345 (H_2L^3), -636346 (H_4L^{10}), -636347 (**2**) and -636348 (**8**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments

We thank Ministerio de Ciencia y Tecnología of Spain (BQU2003-00167) and Xunta de Galicia (PGIDIT06TAM26201PR) for financial support.

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Received: February 12, 2007
Published Online: June 29, 2007