

Formation of Novel 1-D Chains by μ -Amido Bridging of Dinuclear Manganese(III)-Schiff Base Complexes

Manuel R. Bermejo,^{*,[a]} Ana M. González-Noya,^[b] Víctor Abad,^[a] M. Isabel Fernández,^[b] Marcelino Maneiro,^[b] Rosa Pedrido,^[a] and Miguel Vázquez^[a]

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Three novel neutral manganese(III) complexes of stoichiometry $\text{Mn}(\text{R-amsal-3,5-di-}t\text{Bu})(\text{H}_2\text{O})_n$ [$\text{H}_3\text{-R-amsal-3,5-di-}t\text{Bu} = 3\text{-aza-4-(2-hydroxyphenyl)-}N\text{-(2-hydroxyphenyl)but-3-enamide}$; ($\text{R} = \text{H}, 4\text{-Me}, 5\text{-}t\text{Bu}$)] have been synthesised using potentially trianionic and pentadentate Schiff-base ligands containing an amide group. Complexes were thoroughly characterised by elemental analysis, FAB mass spectrometry, infrared spectroscopy, magnetic susceptibility measurements and molar conductivities. Recrystallisation of these complexes from methanol yielded single crystals of $[\text{Mn}_2(\text{amsal-3,5-di-}t\text{Bu})_2(\text{MeOH})_2]_n$ **1**, $[\text{Mn}_2(4\text{-Me-amsal-3,5-di-}t\text{Bu})_2$

$(\text{MeOH})_2]_n$ **2** and $[\text{Mn}_2(5\text{-}t\text{Bu-amsal-3,5-di-}t\text{Bu})_2(\text{MeOH})_2]_n$ **3** with methanol as solvate. Their X-ray characterisation shows that these complexes consist of infinite one-dimensional chains with a repeating cyclic dimeric unit, where the amide oxygen atom is bridging two neighbouring manganese(III) ions. Paramagnetic ^1H NMR spectroscopy confirmed the presence of Mn^{III} in these complexes, while the cyclic voltammetry studies suggest the possibility of obtaining polynuclear Mn^{IV} complexes with this kind of ligand.

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Introduction

In recent years, considerable efforts have been focused on the synthesis and characterisation of polynuclear manganese complexes.^[1] This is mainly because di- or multi-nuclear manganese sites involving oxygen or nitrogen donor ligands are important in the function of enzymes such as alkaline phosphatase,^[2] pseudocatalases,^[3] manganese-based superoxide dismutase (MnSOD)^[4] and the oxygen evolving complex (OEC) of photosystem II.^[5] Moreover, the synthetic complexes have been shown to exhibit a variety of interesting structural and physical properties.^[6]

Recently, we have directed our attention to the coordination chemistry of manganese with Schiff bases containing amide groups. Our interest in this kind of ligands derives from the known ability of ligands containing amide groups to stabilise high oxidation states of metal ions when coordinated with the deprotonated nitrogen atom.^[7–9]

Previously, we succeeded in stabilising the neutral Mn^{III} complexes^[10] with ligands derived from $\text{H}_3\text{-amsal}$ [$\text{H}_3\text{-amsal} = 3\text{-aza-4-(2-hydroxyphenyl)-}N\text{-(2-hydroxyphenyl)but-3-enamide}$] by two methods (an electrochemical synthesis

and the Boucher procedure^[11]). Nevertheless, the low solubilities of these complexes in most common solvents have prevented, until now, their structural characterisation by X-ray diffraction. The knowledge of such structures should improve understanding of ligand design and the synthesis of high oxidation state polymeric manganese complexes.

In order to establish the structural make-up of these complexes, we decided to investigate whether the introduction of *tert*-butyl groups on the aromatic rings of the Schiff base ligands would improve the solubility of the resulting complexes and allow structural characterisation. We have designed some new amide-derived Schiff base ligands in order to prepare novel manganese(III) complexes, and in this paper we report the results.

Results and Discussion

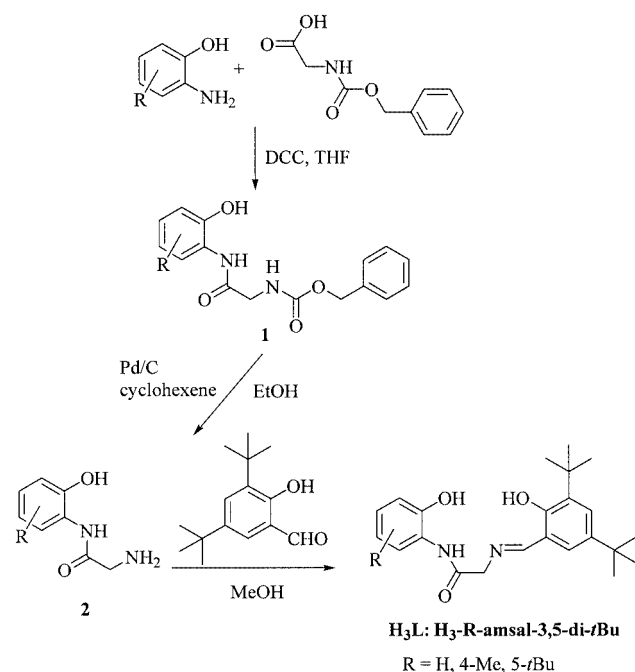
Synthesis and Characterisation of the Ligands

The new unsymmetrical Schiff base ligands reported in this study were prepared in a manner analogous (Scheme 1) with the three-step method to similar ligands described by us previously.^[10]

The first step involves a carbodiimide amide coupling^[12] of *N*-benzyloxycarbonylglycine with 2-hydroxyaniline, 2-hydroxy-4-methylaniline or 2-hydroxy-5-*tert*-butylaniline in THF. This reaction proceeds in excellent yield (see Exp. Sect.) and large quantities of amides **1a**, **1b** or **1c** can be

[a] Departamento de Química Inorgánica, Facultade de Química, Universidade de Santiago de Compostela, 15782 Santiago de Compostela, Spain

[b] Departamento de Química Inorgánica, Facultade de Ciencias, Universidade de Santiago de Compostela, 27002 Lugo, Spain
Fax: (internat.) +34-981-597-525
E-mail: qimb45@usc.es



Scheme 1. Reaction diagram for the preparation of the Schiff-base ligands

prepared. The second step involves the removal of the *Z* protecting group from the amine functionality by sacrificial hydrogenation using cyclohexene and palladium on char-

coal as the catalyst.^[13] This methodology yielded the desired amines **2a**, **2b** or **2c** in high yield and with high purity. Amines **2a**, **2b** and **2c** were then employed as the precursors of the new ligands via conventional condensation reactions with a commercially available substituted salicylaldehyde. The obtained Schiff bases were satisfactorily characterised by elemental analysis, mass spectrometry (Table 1), ¹H NMR (Table 2), ¹³C NMR and IR (Table 3) spectroscopy.

Mass Spectrometry, NMR and IR Spectroscopy

The mass spectra of the ligands each show the peak for H₃L⁺ at 100% intensity (see Table 1), in accord with the proposed formulae.

The ¹H NMR spectroscopic data for the ligands are shown in Table 2. The spectra of H₃-R-amsal-3,5-di-*t*Bu, recorded using [D₆]DMSO as solvent, exhibit a singlet at $\delta \approx 8.6$ ppm assigned to the imine hydrogen atom, corroborating the formation of C=N bonds. The aromatic protons lie in the range $\delta = 6.50$ – 8.03 , while the presence of a singlet at $\delta \approx 4.5$ indicates the presence of the methylene group. Furthermore, all spectra show three singlets in the region of 9.21–13.79 that disappear on deuteration. The peak at higher field was assigned to the NH proton while the two signals at lower field correspond to the OH protons. The spectra of these Schiff bases also show two singlets (for H₃-amsal-3,5-di-*t*Bu and H₃-4-Me-amsal-3,5-di-*t*Bu) or three singlets (for H₃-5-*t*Bu-amsal-3,5-di-*t*Bu) in the range $\delta = 1.2$ – 1.4 , indicating the presence of two or three non-equivalent *tert*-butyl groups, respectively.

Table 1. Analytical and other selected data for the ligands

Ligand	Yield	Colour	M.p. (°C)	MS-EI (<i>m/z</i>)	Analysis (%) ^[a] C	H	N
H ₃ -amsal-3,5-di- <i>t</i> Bu	85%	pale yellow	176	382	72.0 (72.3)	8.0 (7.9)	7.2 (7.3)
H ₃ -4-Me-amsal-3,5-di- <i>t</i> Bu	84%	white	172	396	72.6 (72.7)	8.2 (8.1)	7.1 (7.1)
H ₃ -5- <i>t</i> Bu-amsal-3,5-di- <i>t</i> Bu	87%	white	240	438	73.9 (74.0)	8.8 (8.7)	6.4 (6.4)

^[a] Found (calculated).

Table 2. ¹H NMR spectroscopic data for the ligands in [D₆]DMSO

Ligand ^[b]	Proton ^[a] (a)	(b)	(c)	(d)	(e)	H _{arom}
H ₃ -amsal-3,5-di- <i>t</i> Bu	9.91 (br)	9.30 (s)	4.51 (s)	8.63 (s)	13.70 (s)	6.71–8.03
H ₃ -4-Me-amsal-3,5-di- <i>t</i> Bu ^[c]	9.73 (br)	9.21 (s)	4.51 (s)	8.52 (s)	13.72 (s)	6.50–7.81
H ₃ -5- <i>t</i> Bu-amsal-3,5-di- <i>t</i> Bu ^[d]	9.71 (s)	9.30 (s)	4.52 (s)	8.64 (s)	13.79 (s)	6.73–7.92

^[a] See Scheme 2 for atom labelling. ^[b] Ligands show two singlets at $\delta \approx 1.3$ and 1.4 assigned to the *tert*-butyl groups. ^[c] Includes a singlet at $\delta = 2.10$ assigned to the methyl group. ^[d] Includes a singlet at $\delta = 1.20$ assigned to the *tert*-butyl group.

Table 3. Selected IR bands (in cm^{−1}) for the ligands

Ligand	ν (OH)	ν (NH)	ν (amide I)	ν (CN)	ν (amide II)
H ₃ -amsal-3,5-di- <i>t</i> Bu	3369 (m)	3104 (br)	1657 (s, br)	1639 (sh)	1595 (m)
H ₃ -4-Me-amsal-3,5-di- <i>t</i> Bu	3381 (m)	3105 (br)	1662 (vs)	1633 (s)	1603 (m)
H ₃ -5- <i>t</i> Bu-amsal-3,5-di- <i>t</i> Bu	3385 (m)	3115 (br)	1661 (m)	1628 (vs)	1585 (m)

The ^{13}C NMR spectra of the ligands in $[\text{D}_6]\text{DMSO}$ show signals corresponding to the aromatic carbon atoms (between $\delta = 115$ and 160 ppm), a signal due to the imine

carbon atom (around 165 ppm) and a resonance assigned to the carbonyl carbon atom (around 168 ppm). Additionally, the methylene carbon and the methyl and *tert*-butyl groups, where appropriate, give signals below $\delta = 70$ ppm.

The most significant IR bands for the ligands are recorded in Table 3. They have been assigned by comparison with the IR spectra of the amine precursors and on the basis of our knowledge in this field.^[10a]

Synthesis and Characterisation of Manganese Complexes

The manganese complexes were prepared following a variation of the Boucher method reported by us.^[10c,14]

The brown powdery solid compounds were obtained in high yield via this synthetic route, and appear to be stable in the solid state and in solution. They are moderately soluble in common organic solvents and soluble in polar aprotic coordinating solvents such as DMF and DMSO.

Elemental analyses indicate that these manganese complexes have the general stoichiometry $\text{Mn}(\text{R-amsal-3,5-di-}t\text{Bu})(\text{H}_2\text{O})_4$, suggesting that they are neutral manganese(III) species in which the ligands are tri-deprotonated. Molar conductivity measurements in 10^{-3} M DMF solutions, in the range $3\text{--}9\ \mu\text{S cm}^{-1}$, show the non-electrolytic behaviour of these complexes.^[15]

Mass Spectrometry and IR Spectroscopy

Fast atom bombardment (FAB) mass spectra contain peaks relating to fragments of the form $[\text{MnL}]^+$, indicating ligand coordination to the metal centre. Furthermore, these

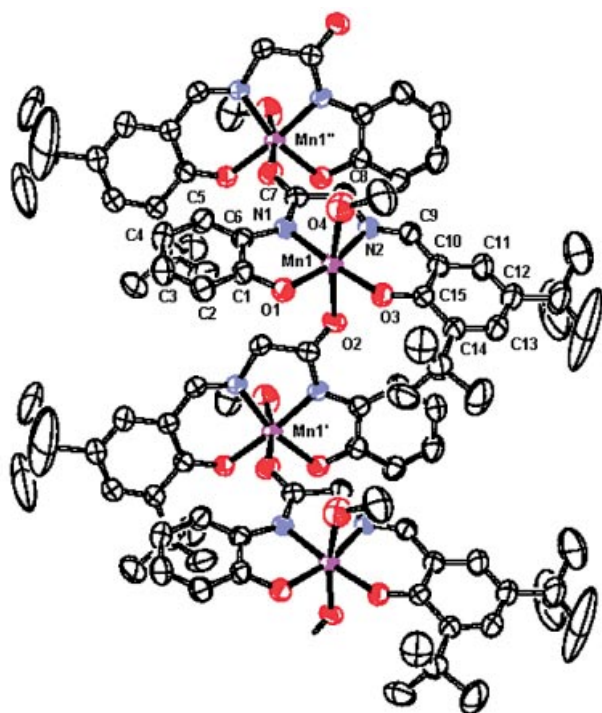


Figure 1. An ORTEP view of the crystal structure of $[\text{Mn}_2(\text{amsal-3,5-di-}t\text{Bu})_2(\text{MeOH})_2]_n$ (**1**); ellipsoids are drawn at 50% probability; symmetry operations: ' : $-x + 1, y - 1/2, -z + 1/2$; '' : $-x + 1, y + 1/2, -z + 1/2$

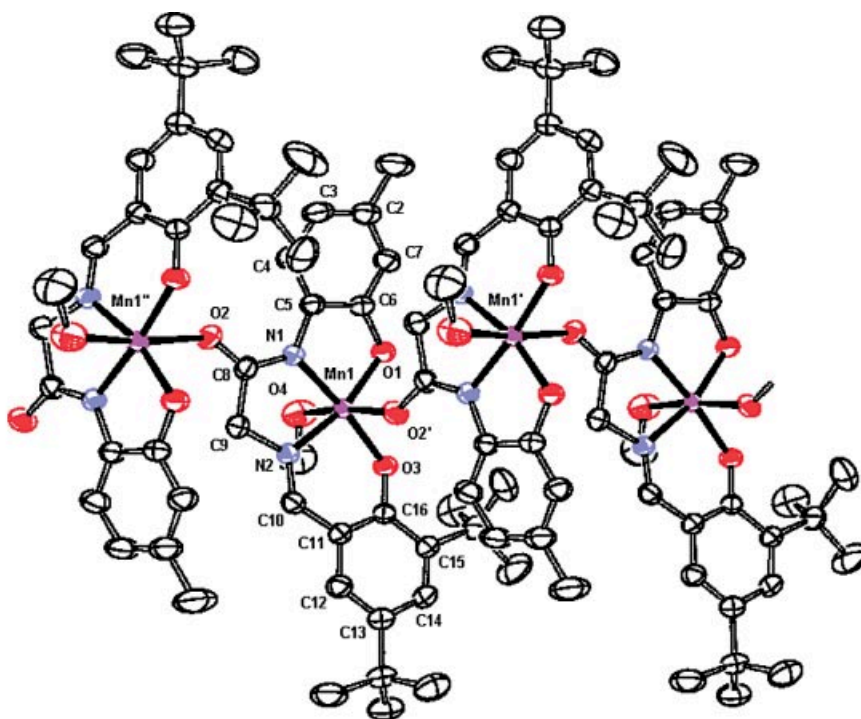


Figure 2. An ORTEP view of the crystal structure of $[\text{Mn}_2(4\text{-Me-amsal-3,5-di-}t\text{Bu})_2(\text{MeOH})_2]_n$ (**2**); ellipsoids are drawn at 50% probability; symmetry operations: ' : $-x + 1, y + 1/2, -z + 1/2$; '' : $-x + 1, y - 1/2, -z + 1/2$

spectra exhibit peaks due to the fragment $[\text{Mn}_2\text{L}_2]^+$, which can be attributed tentatively to the presence of dimeric/polymeric species in the solid state.

The ligand coordination to the metal centre is also supported by the IR spectra, which are very similar for all the complexes. Thus, a band at about 1620 cm^{-1} , attributable to $\nu(\text{CN})$, shifted to lower energy compared with the free ligands values, indicating the coordination of the ligand to the metal through the imine nitrogen atom. This $\nu(\text{CN})$ band is strong and broad and it obscures the amide I and amide II bands. Additionally, bands centred at ca. 3400 cm^{-1} can be observed in these spectra, in accordance with the presence of coordinated and/or lattice water or methanol.

Finally, the absence of a strong band at ca. 1100 cm^{-1} confirms the absence of perchlorate anions in these manganese complexes.

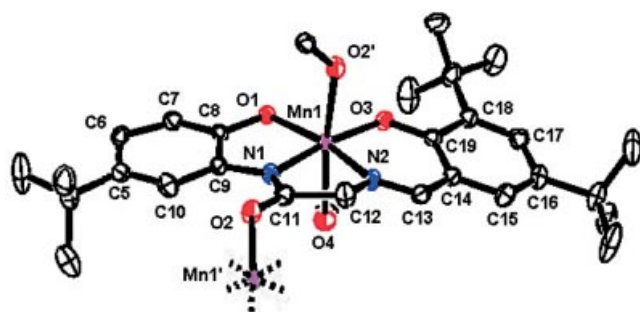


Figure 3. An ORTEP view of the environment around the manganese centre for $[\text{Mn}_2(5\text{-}i\text{Bu-amsal-3,5-di-}i\text{Bu})_2(\text{MeOH})_2]_n$ (**3**); ellipsoids are drawn at 50% probability

X-Ray Diffraction Studies

Crystal Structures of Complexes **1**, **2** and **3**

Single crystals of $[\text{Mn}_2(\text{amsal-3,5-di-}i\text{Bu})_2(\text{MeOH})_2]_n$ (**1**), $[\text{Mn}_2(4\text{-Me-amsal-3,5-di-}i\text{Bu})_2(\text{MeOH})_2]_n$ (**2**) and $[\text{Mn}_2(5\text{-}i\text{Bu-amsal-3,5-di-}i\text{Bu})_2(\text{MeOH})_2]_n$ (**3**) suitable for X-ray diffraction studies were grown as detailed in the Exp. Sect. These analyses show that **1**, **2** and **3** have similar structures that consist of a polymeric chain of repeating dimeric units. These dimeric units contain two ligand units, two manganese centres and two molecules of methanol. Furthermore, complexes **1**, **2** and **3** contain methanol as solvate. Complexes **1** and **2** crystallise in the orthorhombic space group $Pbca$, while complex **3** crystallises in the monoclinic space group $C2/c$. The ORTEP diagrams for **1** and **2** are shown in Figure 1 and Figure 2, respectively. The ORTEP view of the environment of the manganese atom for complex **3** is shown in Figure 3. Experimental details are given in Table 4 and selected bond lengths and angles in Table 5.

The geometry around each Mn atom can be described as distorted octahedral, where the trianionic and pentadentate ligand coordinates the Mn^{III} centre with the two phenol O-atoms [O(1), O(3)], the imine N-atom [N(2)] and the amide N-atom [N(1)] occupying the equatorial positions (see Figure 3). The coordination sphere around each manganese centre is then completed by a capping methanol molecule [O(4)] and an amide O-atom [O(2')] from the neighbouring complex molecule. Thus, the amide oxygen atom [O(2)] of one ligand is coordinated to the manganese ion of the neighbouring molecule, acting as a bridge, which generates an infinite one-dimensional chain $\text{Mn}-\text{O}_{\text{amide}}(\text{L})-\text{Mn}-\text{O}'_{\text{amide}}(\text{L})$ resulting in a $\text{Mn}\cdots\text{Mn}$ distance of $6.064\text{ \AA}$ for **1**, $6.120\text{ \AA}$ for **2**, and $6.035\text{ \AA}$ for **3**.

Table 4. Crystal data and details of refinement for the complexes **1**, **2** and **3**

	1	2	3
Empirical formula	$\text{C}_{25}\text{H}_{34}\text{MnN}_2\text{O}_5$	$\text{C}_{26}\text{H}_{36}\text{MnN}_2\text{O}_5$	$\text{C}_{29}\text{H}_{43}\text{MnN}_2\text{O}_5$
Molecular mass	497.49	511.52	554.59
Temperature [K]	293(2)	293(2)	110(2)
Wavelength [nm]	0.71073	0.71073	0.71073
Crystal system	orthorhombic	orthorhombic	monoclinic
Space group	$Pbca$	$Pbca$	$C2/c$
a [$\text{\AA}$]	18.653(3)	19.572(3)	37.646(10)
b [$\text{\AA}$]	8.8588(14)	8.8073(12)	7.2783(19)
c [$\text{\AA}$]	32.470(6)	32.192(4)	23.023(6)
α [$^\circ$]	90.00	90.00	90.00
β [$^\circ$]	90.00	90.00	108.256(5)
γ [$^\circ$]	90.00	90.00	90.00
Z	8	10	8
Absorption coefficient [mm^{-1}]	0.513	0.511	0.478
Crystal size [mm^3]	$0.82 \times 0.42 \times 0.06$	$0.44 \times 0.33 \times 0.18$	$0.13 \times 0.17 \times 0.13$
Reflections collected	29618	34239	18487
Independent reflections	5928 [$R(\text{int}) = 0.0577$]	6310 [$R(\text{int}) = 0.0537$]	6759 [$R(\text{int}) = 0.0344$]
Final R int [$I > 2\sigma(I)$]	$R1 = 0.0711$ $wR2 = 0.1818$	$R1 = 0.0447$ $wR2 = 0.1225$	$R1 = 0.0525$ $wR2 = 0.1044$
R int (all data)	$R1 = 0.1302$ $wR2 = 0.2237$	$R1 = 0.0910$ $wR2 = 0.1662$	$R1 = 0.1173$ $wR2 = 0.1299$

Table 5. Selected bond lengths [Å] and angles [°] for the complexes **1**, **2** and **3**

	1	2	3
Mn1–O3 _{phenol}	1.881(3)	1.8913(18)	1.875(2)
Mn1–O1 _{phenol}	1.916(3)	1.9198(19)	1.930(2)
Mn1–N1 _{amide}	1.939(4)	1.942(2)	1.933(3)
Mn1–N2 _{imine}	1.964(4)	1.963(2)	1.958(3)
Mn1–O2' _{amide}	2.321(3)	2.349(2)	2.242(3)
Mn1–O4 _{methanol}	2.275(5)	2.281(2)	2.270(4)
O2=C _{amide}	1.247(6)	1.247(3)	1.248(4)
Mn1...Mn1'	6.064	6.120	6.035
O3–Mn1–O1	103.33(15)	104.01(8)	104.35(10)
O1–Mn1–N1	82.87(15)	83.31(9)	83.44(11)
O3–Mn1–N2	92.15(16)	91.21(9)	91.36(11)
N1–Mn1–N2	81.64(16)	81.48(9)	80.84(12)
O4–Mn1–O2'	171.60(17)	173.34(8)	173.93(9)

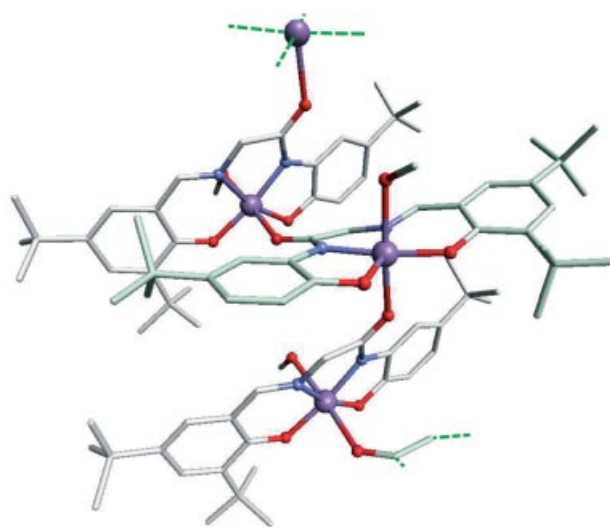
It is well known that Mn^{III} complexes are able to form dimeric or polymeric species through different coordinative bridges:^[14,16] μ -Oxo, μ -phenoxo, μ -aquo, μ -carboxylate, μ -cyanide, μ -thiocyanate, etc. μ -oxo and μ -phenoxo bridges generate dimeric structures; μ -carboxylate, μ -cyanide and μ -thiocyanate usually yield polymeric species, while the μ -aquo ligand can generate both dimeric or polymeric structures. The distance Mn...Mn for the complexes reported herein are longer than the corresponding distances in μ -oxo, μ -phenoxo or μ -aquo Mn^{III} complexes, and shorter than the distances found for μ -carboxylate Mn^{III} complexes. On the other hand, ionic metal(II) complexes with amide ligands where oxygen amide atoms behave as bridges have been reported.^[17] However, to the best of our knowledge, the type of compound reported in the present case, with Mn^{III}, has not been described previously in the literature.

The bond distances in the equatorial plane Mn–N [ranging from 1.933 to 1.964 Å] and Mn–O [in the range 1.875–1.930 Å] are typical of manganese(III) complexes^[16,18] and corroborate complete deprotonation of the ligands. The distances Mn–O4_{methanol} [2.270–2.281 Å] are in agreement with other previous results,^[18] and are longer than the axial distances Mn–O2'_{amide}, except for complex **3**. The distances O2=C_{amide} (ca. 1.247) are longer than those found for the related free ligands (ca. 1.235),^[10a] as expected. The axial Mn–O distances are considerably longer than the equatorial Mn–O bond lengths quoted above, indicating that the Jahn–Teller elongation expected for a high-spin d⁴ manganese(III) ion is present along the chain of these polymers.

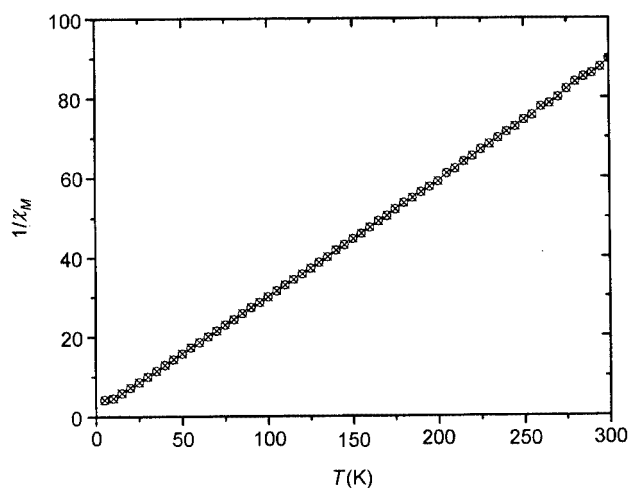
The deviation from an ideal octahedral geometry is also revealed by the range of angles observed around the metal centre [from 80.84 to 104.35°], as well as by the interaxial angle O4–Mn1–O2' of ca. 173°. The slight deviation of the equatorial plane from planarity further reinforces this distortion (maximum deviation from the calculated least-squares plane formed by O1, N1, N2 and O3 is ca. 0.004 Å for **1**, 0.009 Å for **2** and 0.025 Å for **3**, with the manganese atoms lying out of this plane by ca. 0.011 Å for **1**, 0.006

Å for **2** and 0.025 Å for **3**). These planes also present a gauche conformation.

These ligands are expected to show a high degree of planarity owing to the conjugation and presence of only one sp³ atom in the chelate rings (named as C8 for **1**, C9 for **2** and C12 for **3** in Figures 1, 2 and 3, respectively). In fact, the angles between calculated chelate planes present values of 0.81° and 4.43° for **1**, 2.90° and 7.68° for **2**, and the highest values for **3** (10.87° and 14.91°).

Figure 4. Part of the polymeric 1–D chain of **3**, showing the zigzag disposition of the manganese centres (in violet)

It is interesting to note that these infinite chains are not linear (see Figure 4), as the manganese atoms are situated in a zigzag arrangement. The angles between neighbouring manganese atoms (Mn1'–Mn1–Mn1'') are 93.85° for **1**, 92.03° for **2** and 74.17° for **3**. The head-to-tail arrangement of the ligands allows coordination of the amide oxygen atom of each unit to the metal ion of the next unit in the chain.

Figure 5. Thermal dependence of $1/\chi_M$ for **2**

Magnetic Studies

The study of room temperature magnetic properties for the complexes shows that their magnetic moments (see Exp. Sect.) are all close to the spin-only value of 4.9 BM, expected for a magnetically dilute octahedral high-spin d^4 manganese(III) ion.

Variable temperature magnetic susceptibility of the complexes were measured in the temperature range 5–300 K using a small applied field of 5000 G. Plots of the reciprocals of the magnetic susceptibilities against absolute temperature are linear, so that all the complexes obey the Curie–Weiss law. An example is shown in Figure 5 for complex 2.

The magnetic behaviours of complexes 1, 2 and 3 are identical and can be illustrated by the thermal variation of the $\chi_M T$ versus T plot for complex 2 as in Figure 6. The $\chi_M T$ product is practically constant in the 300–100 K range with an observed value ($3.34 \pm 0.3 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$) corresponding to the value expected for an isolated high-spin Mn^{III} cation. On further reduction of the temperature, this value decreases smoothly down to $2.99 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ at 30 K, and then more steeply to reach a value of $1.17 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ at 5 K.

We attempted theoretical calculations to reproduce, and for comparison with, the experimental results. For an infinite chain of 4/2 local spins the simpler analytical ex-

pression that may be used to fit the experimental data derives from Fisher's expression:^[19]

$$\chi T = [Ng^2\beta^2 S(S+1)/3k] \{ (1+u)/(1-u) \} \text{ where } u = \coth[-2JS(S+1)/kT] - [kT/2JS(S+1)]$$

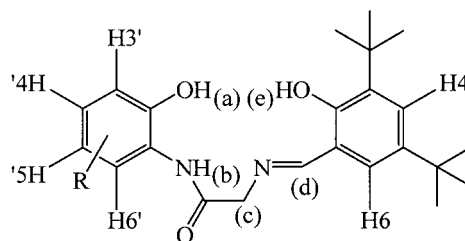
The best agreement between experimental and calculated data from 300 to 5 K corresponds to $J = -0.3 \text{ cm}^{-1}$ and $g = 2.05$ with an agreement factor $R (= \Sigma[(\chi_M T)_{\text{obsd.}} - (\chi_M T)_{\text{calcd.}}]^2 / \Sigma[(\chi_M T)_{\text{obsd.}}]^2)$ of $3.4 \cdot 10^{-4}$.

This study indicates little or no antiferromagnetic interaction between neighbouring metal centres in the solid state. Therefore, we can interpret the magnetic properties of these Mn^{III} polymer complexes as ordinary paramagnetic^[19] and this is in agreement with the intermolecular $\text{Mn} \cdots \text{Mn}$ distances of about 6 Å.

^1H NMR Spectroscopy

Paramagnetic ^1H NMR spectra for the complexes were recorded in $[\text{D}_6]\text{DMSO}$ at room temperature. The data are presented in Table 6.

The spectra obtained for these complexes contain three or four proton resonances that lie outside the diamagnetic region ($\delta = 0\text{--}14$). The interpretation of these data is based on the findings of Pecoraro and co-workers^[21] and also on our own results^[10a,10b,22] for other Mn^{III} complexes with related Schiff base ligands. The protons *ortho* to the ring position occupied by a Mn-coordinated atom H3', H6 and H6' (see Scheme 2), were not observed.



Scheme 2. Hydrogen atom labelling of the ligands for the ^1H NMR studies

Two or three relatively sharp peaks are observed upfield between $\delta = -14$ and -32 ppm , which we have assigned to the H4 protons of the aldehyde and to H4' and H5' protons of the amine.^[10a,10b,21,22] The comparison between the spec-

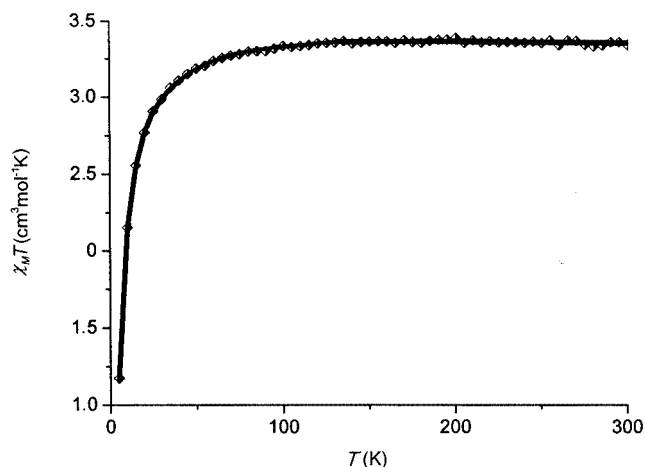


Figure 6. Thermal dependence of $\chi_M T$ for 2; the full line (—) corresponds to the best data fit

Table 6. ^1H NMR and electrochemical data for the complexes

Complex	^1H NMR			$-\text{CH}_2-$	E_{ox}/V	Redox potentials ^[a]	
	H4	H4'	H5'			E_{red}/V	Peak
1	−31.95	−14.80	−25.90	35.90	— 0.778	−0.278 —	R1 O2
2	−31.50	na ^[b]	−27.08	34.46	— 0.690	−0.282 —	R1 O2
3	−32.07	−18.42	na	30.42	— 0.700	−0.286 0.602	R1 O2,R2

^[a] Potentials vs. SCE. ^[b] na = not applicable.

tra of these three complexes, with substitution of the H4' and H5' positions of the amine ring, provides an indication of the appropriate assignments. Clearly the upfield peaks at $\delta \approx -32$ correspond to the H4 protons. The features at $\delta = -14.80$ and -18.42 arise from H4' protons, while the downfield resonances at $\delta = -25.90$ and -27.08 arise from H5' protons.

Additionally, one broad peak observed downfield ($\delta = 30\text{--}36$) can be assigned to the aliphatic protons in the methylene bridge between the imine and amide nitrogen atoms.

It is well known that high-spin Mn^{III} complexes in an octahedral field show isotropically shifted ^1H NMR spectra arising from ligand protons.^[23] Therefore, the data obtained from these NMR studies serve to corroborate the formation of these novel manganese(III) complexes.

Electrochemical Behaviour of the Complexes

Cyclic voltammograms of all the complexes were obtained from dimethylformamide solutions at slow scan rates of 0.02 V s^{-1} over a potential range from $+1$ to -1 V . The numerical data are given in Table 6 and a typical voltammogram is shown in Figure 7.

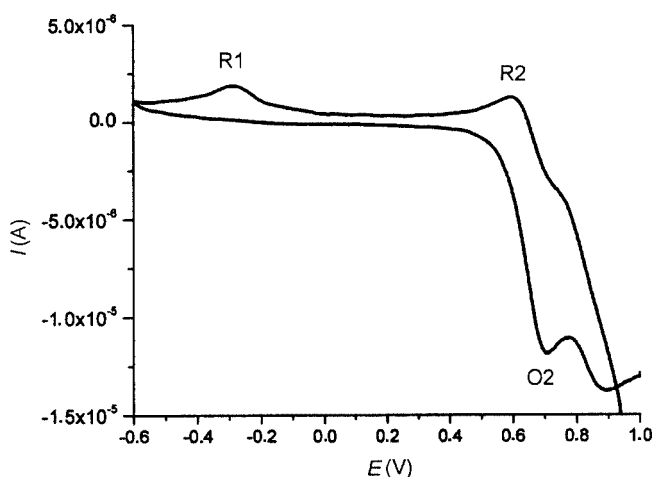


Figure 7. Cyclic voltammetry for 3

All the complexes behave similarly. All voltammograms display an irreversible process at negative potentials (quoted as R1 in Table 6), which we assign to the reduction of manganese(III) to manganese(II).^[14,24]

On the other hand, a second redox process assigned to the oxidation of manganese(III) to manganese(IV) is present at positive potentials for all the complexes (quoted as O2 in Table 6). This redox wave is irreversible for **1** and **2**, but for **3** presents an important rate of reversibility (R2, see Figure 7).

It is interesting to note that the presence of the methyl or *tert*-butyl groups on the aromatic ring of the amine precursor decreases this oxidation potential as it does with related ligands.^[25] Hence, it seems obvious that manganese(IV) could be stabilised by this kind of ligand, containing hard

donor atoms, especially if an electron-donating substituent were to be introduced.^[7a,7b,8a,8b]

We found that the complexes exhibit low current intensities in their redox waves. This behaviour is attributed to the polymeric nature of these complexes, which results in a lower diffusion coefficient.^[26]

Conclusion

Self-assembly of manganese ions with the novel unsymmetrical and potentially trianionic pentadentate amide group-containing Schiff base ligands, leads to neutral, polymeric manganese(III) complexes. The X-ray crystal structures of these complexes show that the oxygen amide atom of these ligands can act as a bridge between neighbouring manganese atoms and afford zigzag one-dimensional chains, previously unreported for manganese(III) ions. In addition, the observations reported here could be helpful for the study of biological systems, in which relatively weak but cooperative interactions between sets of metal ions and linked amide groups are present.

Finally, it seems that this kind of ligand is suitable for stabilization of Mn^{III} complexes, and could have potential in the synthesis of polynuclear Mn^{IV} complexes.

Experimental Section

General: Starting materials were purchased from Aldrich except manganese(II) perchlorate hexahydrate (Fluka) and cyclohexene (Panreac) and were used without further purification.

Elemental analyses were performed on a Carlo Erba EA 1108 analyser. NMR spectra were recorded on a Bruker WM-250 spectrometer using $[\text{D}_6]\text{DMSO}$ as solvent; δ = chemical shift in ppm; s = singlet, d = doublet, t = triplet, m = multiplet, br = broad. Infrared spectra were recorded as KBr pellets on a Bruker UFS-66V spectrophotometer in the range $4000\text{--}600\text{ cm}^{-1}$. The bands are reported as: vs = very strong, s = strong, m = medium, w = weak, sh = shoulder, and br = broad. Mass spectrometry (Electronic Impact) was performed on a Hewlett–Packard 5988A mass spectrometer, whilst fast atom bombardment (FAB) was done on a Micromass AutoSpec mass spectrometer, employing *m*-nitrobenzyl alcohol as the matrix. Magnetic susceptibility measurements in the $5\text{--}300\text{ K}$ temperature range were performed using a SQUID magnetometer operating at 5000 G . Room temperature magnetic susceptibilities were measured using a Digital Measurement system MSB-MKI, calibrated using tetrakis(isothiocyanato)cobaltate(II). Conductivities were obtained at $25\text{ }^\circ\text{C}$ from 10^{-3} M solutions in DMF on a Philips PW9526 instrument. Cyclic voltammetry was performed by using an EG&G PAR model 273 potentiostat, controlled by the EG&G PAR model 270 software, in conjunction with a three-electrode cell, fitted with a purge gas inlet and outlet, consisting of a graphite disc working-electrode, a saturated calomel reference electrode and a platinum auxiliary electrode. Voltammograms were obtained from ca. 10^{-3} M dimethylformamide solutions of the metal complexes containing 0.1 M tetraethylammonium perchlorate as supporting electrolyte.

Syntheses

Preparation of Schiff Base Ligands: Ligands were prepared according to a three-step method previously reported by us^[10] and which is shown in Scheme 1.

First Step. Synthesis of Precursors 1a, 1b and 1c

***N*-(2-Hydroxyphenyl)-2-[(phenylmethoxy)carbonylamino]ethanamide (1a):** 2-Hydroxyaniline (2.61 g, 23.9 mmol) and a slight excess of *N,N'*-dicyclohexylcarbodiimide (5.3 g, 25.7 mmol) was added to a solution of *N*-benzyloxycarbonylglycine (5 g, 23.9 mmol) in THF (100 mL). This mixture was stirred at room temperature for four hours.^[12] The insoluble *N,N'*-dicyclohexylurea was removed by filtration and the solvent replaced by ethyl acetate (100 mL). Addition of petroleum ether (b.p. 40–60 °C) afforded 6.46 g (90%) of the amine **1a**. M.p. 172 °C. ¹H NMR (250 MHz, [D₆]DMSO): δ = 4.06 (d, 2 H), 5.30 (s, 2 H), 6.96 (m, 1 H), 7.56 (m, 5 H), 7.91 (t, 1 H), 8.09 (d, 1 H), 9.31 (s, 1 H), 10.09 (s, 1 H) ppm. IR (KBr): $\tilde{\nu}$ = 3392 (s, OH), 3270 and 3075 (both s, NH), 1677 (vs, amide I), 1618 (s, amide II) cm⁻¹. EI-MS: m/z = 300.1. C₁₆H₁₆N₂O₄ (300.0): calcd. C 64.0, H 5.4, N 9.3; found C 64.1, H 5.5, N 9.4.

***N*-(2-Hydroxy-4-methylphenyl)-2-[(phenylmethoxy)carbonylamino]ethanamide (1b):** Preparation as described above, using 2-hydroxy-4-methylaniline (2.95 g, 23.9 mmol). Yield 6.78 g (90%). M.p. 185 °C. ¹H NMR (250 MHz, [D₆]DMSO): δ = 2.43 (s, 3 H), 4.07 (d, 2 H), 5.30 (s, 2 H), 6.82 (d, 1 H), 6.92 (s, 1 H), 7.60 (m, 5 H), 7.94 (t, 1 H), 7.97 (s, 1 H), 9.30 (s, 1 H), 9.99 (s, 1 H) ppm. IR (KBr): $\tilde{\nu}$ = 3392 (s, OH), 3269 and 3076 (both s, NH), 1677 (vs, amide I), 1618 (s, amide II) cm⁻¹. EI-MS: m/z = 314.1. C₁₇H₁₈N₂O₄ (314.0): calcd. C 65.0, H 5.8, N 8.9; found C 65.1, H 6.0, N 9.1.

***N*-(2-Hydroxy-5-*tert*-butylphenyl)-2-[(phenylmethoxy)carbonylamino]ethanamide (1c):** Preparation as described above, using 2-hydroxy-5-*tert*-butylaniline (3.95 g, 23.9 mmol). Yield 6.4 g (75%). M.p. 185 °C. ¹H NMR (250 MHz, [D₆]DMSO): δ = 1.30 (s, 9 H), 3.88 (d, 2 H), 5.09 (s, 2 H), 6.80 (d, 1 H), 6.96 (d, 1 H), 7.37 (m, 5 H), 7.71 (t, 1 H), 7.92 (s, 1 H), 9.15 (s, 1 H), 9.66 (s, 1 H) ppm. IR (KBr): $\tilde{\nu}$ = 3390 (s, OH), 3268 (s, NH), 3077 (m, NH), 1678 (vs, amide I), 1617 (s, amide II) cm⁻¹. EI-MS: m/z = 356.1. C₂₀H₂₄N₂O₄ (356.0): calcd. C 67.4, H 6.8, N 7.9; found C 67.5, H 6.9, N 7.8.

Second Step. Synthesis of precursors 2a, 2b and 2c

2-Amino-*N*-(2-hydroxyphenyl)ethanamide (2a): A solution of **1a** (2 g, 6.7 mmol) in ethanol (100 mL) was mixed with cyclohexene (5 mL, in excess to the molar proportion required) and commercial 10% Pd–C catalyst (0.50 g; catalyst:substrate ratio 1:4 by weight).^[13] The mixture was refluxed for 15 min. The catalyst was removed by filtration and washed with ethanol, and the combined filtrates were evaporated under reduced pressure to give the deprotected amine **2a**. Yield 1.05 g (95%). M.p. 148 °C. ¹H NMR (250 MHz, [D₆]DMSO): δ = 3.26 (s, 2 H), 6.77 (m, 1 H), 6.88 (s, 1 H), 6.89 (s, 1 H), 8.18 (d, 1 H) ppm. IR (KBr): $\tilde{\nu}$ = 3431 (s, OH), 3420 and 3252 (both s, NH₂), 3083 (s, br, NH), 1649 (vs, amide I), 1614 (s, amide II) cm⁻¹. EI-MS: m/z = 166.0. C₈H₁₀N₂O₂ (166.0): calcd. C 57.8, H 6.1, N 16.9; found C 57.5, H 6.2, N 16.6.

2-Amino-*N*-(2-hydroxy-4-methylphenyl)ethanamide (2b): Preparation as described above, using **1b** (2 g, 6.36 mmol). Yield 1.09 g (95%). M.p. 175 °C. ¹H NMR (250 MHz, [D₆]DMSO): δ = 2.12 (s, 3 H), 3.17 (s, 2 H), 6.49 (d, 1 H), 6.61 (d, 1 H), 7.49 (d, 1 H) ppm. IR (KBr): $\tilde{\nu}$ = 3356 (s, OH), 3278 (s, NH₂), 3046 (s, br, NH), 1655 (vs, amide I), 1606 (s, amide II) cm⁻¹. EI-MS: m/z = 180.1.

C₉H₁₂N₂O₂ (180.0): calcd. C 60.0, H 6.7, N 15.6; found C 60.3, H 6.9, N 15.5.

2-Amino-*N*-(2-hydroxy-5-*tert*-butylphenyl)ethanamide (2c): Preparation as described above, using **1c** (2 g, 5.61 mmol). Yield 1 g (80%). M.p. 210 °C. ¹H NMR (250 MHz, [D₆]DMSO): δ = 0.91 (s, 9 H), 3.12 (s, 2 H), 6.55 (d, 1 H), 6.69 (d, 1 H), 8.03 (s, 1 H) ppm. IR (KBr): $\tilde{\nu}$ = 3380 (vs, OH), 3270 (vs, NH₂), 3065 (m, NH), 1650 (vs, amide I), 1610 (s, amide II) cm⁻¹. EI-MS: m/z = 222.1. C₁₂H₁₈N₂O₂ (222.0): calcd. C 64.9, H 8.1, N 12.6; found C 64.6, H 8.1, N 12.7.

Third Step. Preparation of Schiff Base Ligands: The Schiff-base ligands were prepared in a standard manner by the reaction of equimolecular quantities of 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde and the appropriate amines **2a**, **2b** or **2c**, which is typified by the preparation of H₃-5-*t*Bu-amsal-3,5-di-*t*Bu. The amine **2c** (0.5 g, 2.25 mmol) and the salicylaldehyde (0.53 g, 2.25 mmol) were dissolved in methanol (100 mL) and the solution was brought to reflux. The volume of the solution was reduced over a three hour period to ca. 50 mL, using a Dean–Stark trap and was then allowed to cool. The solid, which precipitated, was collected by filtration, washed with diethyl ether (3 mL) and dried in vacuo. The purity of the ligands was checked by elemental analysis, mass spectrometry (Table 1), ¹H NMR (Table 2), ¹³C NMR and IR (Table 3) spectroscopy.

Synthesis of the Complexes

All of the manganese complexes were obtained using the same procedure. A typical preparation is outlined below.

Mn(amsal-3,5-di-*t*Bu)(H₂O)₄: A solution of NaOH (0.03 g, 0.78 mmol) in water (3 mL) was added to a solution of the ligand H₃-amsal-di-*t*Bu (0.1 g, 0.26 mmol) in methanol (15 mL). Manganese(II) perchlorate hexahydrate (0.15 g, 0.41 mmol) in 5 mL of methanol was then added and a rapid change of solution colour was observed, from yellow to brown. (**CAUTION:** All perchlorates are potentially explosive. Although no problems have been encountered during this study, care should be taken in the handling and treatment of these materials). After stirring at room temperature in the presence of air for 12 h, the solid formed was collected by filtration, washed with hexane and dried in vacuo. Yield 80%. C₂₃H₃₅MnN₂O₇ (505.9): calcd. C 54.6, H 6.9, N 5.5; found C 54.8, H 6.7, N 5.3. MS(FAB): m/z (%) = 434 (100, MnL), 869 (12, Mn₂L₂). Magnetic moment μ_{eff} = 5.0 B. M. Conductivity (in DMF) Λ_{M} = 3 $\mu\text{S cm}^{-1}$.

Recrystallisation of the dark brown powder from methanol by slow evaporation afforded brown crystals of [Mn₂(amsal-3,5-di-*t*Bu)₂(MeOH)₂]_n **1**, suitable for X-ray diffraction studies.

Mn(4-Me-amsal-3,5-di-*t*Bu)(H₂O)₂: Yield 65%. C₂₄H₃₃MnN₂O₅ (483.9): calcd. C 59.5, H 6.8, N 5.8; found C 60.1, H 6.6, N 5.5. MS(FAB): m/z (%) = 449 (100, MnL), 898.1 (16, Mn₂L₂). Magnetic moment μ_{eff} = 5.1 B. M. Conductivity (in DMF) Λ_{M} = 3 $\mu\text{S cm}^{-1}$. Recrystallisation of the brown powder in methanol yielded crystals of [Mn₂(4-Me-amsal-3,5-di-*t*Bu)₂(MeOH)₂]_n **2**, suitable for X-ray analyses.

Mn(5-*t*Bu-amsal-3,5-di-*t*Bu)(H₂O)₄: Yield 70%. C₂₇H₄₃MnN₂O₇ (561.9): calcd. C 57.7, H 7.7, N 5.0; found C 58.1, H 7.5, N 5.0. MS(FAB): m/z (%) = 490.3 (100, MnL), 981.6 (18, Mn₂L₂). Magnetic moment μ_{eff} = 4.9 B. M. Conductivity (in DMF) Λ_{M} = 9 $\mu\text{S cm}^{-1}$.

Recrystallisation of the brown powder in methanol yielded crystals of [Mn₂(5-*t*Bu-amsal-3,5-di-*t*Bu)₂(MeOH)₂]_n **3**, suitable for X-ray studies.

Crystallographic Measurements

Crystals of **1**, **2** and **3** suitable for single-crystal X-ray studies were obtained as described above. Data were collected at 293 K for **1** and **2**, and at 120 K for **3** on a Bruker SMART 1000 diffractometer, employing graphite-monochromated MoK α ($\lambda = 0.71073$ Å) radiation. The structures were solved by direct methods^[26] and finally refined by full-matrix least-squares based on F^2 . An empirical absorption correction was applied using SADABS.^[27] Non-hydrogen atoms were anisotropically refined. Hydrogen atoms were included in the structure factor calculation in idealised positions.

CCDC-228228 (for **1**), -228227 (for **2**) and -228226 (for **3**) 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.) +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

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