A direct route to obtain manganese(III) complexes with a new class of asymmetrical Schiff base ligands

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A new class of asymmetrically substituted Schiff base ligands has been synthesised incorporating hard amido donor atoms. The single crystal X-ray structure of one of these ligands, H_3-amsal, has been determined [H_3-amsal = 3-aza-4-(2-hydroxyphenyl)-*N*-(2-hydroxyphenyl)but-3-enamide]. The structure reveals the ligand to be suitable for use as an equatorially co-ordinating ligand in octahedral complexes. A new route to obtaining manganese(III) complexes of these ligands, with high yield and purity, has been designed. Complexes of the form Mn^{III}(amsal-R)$(H_2O)_n$ ($n = 1$–4) have been prepared by the electrochemical oxidation of a manganese anode in an acetonitrile solution of the ligands. The compounds have been characterised by elemental analyses, IR and ^1H NMR spectroscopies, FAB mass spectrometry, magnetic measurements, Λ_M and cyclic voltammetry.

The co-ordination chemistry of manganese with a diverse range of ligands remains an area of considerable interest. This is not only because of the relevance that a number of model manganese complexes have to biological systems,[1] but also due to the fascinating cluster compounds, which exhibit unusual magnetic properties, and the elegant supramolecular arrays that have been discovered.[2] In addition to the interest from this inorganic standpoint, there is also considerable interest in the application of manganese complexes in organic synthesis due to their potent catalytic properties, particularly in the asymmetric epoxidation of certain olefins.[3]

Our interest in this area has centred for a considerable time on the investigation of the co-ordination chemistry of manganese with a range of symmetrical and asymmetrical Schiff base ligands. There are principally two synthetic methods that we have used in trying to prepare manganese(III) complexes of these ligands. The first involves the classical aerobic oxidation procedure of Boucher and Coe.[4] Although we have had considerable success with this methodology, there are frequently intractable problems associated with this route, particularly the formation of large quantities of insoluble materials when poorly co-ordinating anions, such as perchlorate, are employed. Furthermore, there are occasionally problems associated with the integrity of the oxidation state in the resultant complexes, depending on the nature of the substituents on the phenyl rings of the Schiff base ligand.[5] The second method, which is considerably less explored, involves the synthesis of the complexes using an electrochemical cell in which a manganese anode is oxidised with concomitant cathodic reduction of the ligand. In contrast to the Boucher methodology, this route generally gives very clean reactions from which manganese(II) complexes are generally isolated.[6] Occasionally we have isolated cationic manganese(III) species[7] in which the complex anion results from the supporting electrolyte; however, these examples are rare and the expected oxidation level from this procedure is manganese(II).

We were keen to investigate the viability of the electrochemical methodology further for the preparation of new manganese(III) complexes routinely and to investigate whether higher oxidation states of manganese can be accessed *via* this synthetic route, in view of the role that these higher oxidation states play in natural systems, such as the oxygen evolving complex of green plant photosynthesis and the putative oxomanganese(V)salen species implicated in the Jacobsen–Katsuki epoxidation. Complexes of manganese in oxidation states higher than (IV) are rare,[8] particularly with biologically relevant ligands. Okawa *et al.*[9] reported the preparation of what were assigned as manganese(IV) and (V) complexes using amido donors to stabilise the high valent metal ion. However, owing to the severe insolubility problems associated with these complexes, no solution or single crystal data were presented. Irrefutable evidence of the isolation of manganese(V) amido complexes has been provided by Collins and Gordon–Wylie,[10] who have extensively characterised several species by single crystal X-ray diffraction and solution ^1H NMR. It is thus clear that such ligands are capable of stabilising high oxidation states.

In view of the diverse and interesting co-ordination chemistry we have previously encountered when we have employed asymmetrical ligands, together with the potential of amido donors to stabilise higher oxidation states of manganese, we decided that it was of interest to incorporate an amido donor into an asymmetrical Schiff base ligand and investigate whether higher oxidation states of manganese could be accessed using electrochemical synthetic methodology. We report herein a preparative method to obtain Mn(III) complexes with new asymmetrical Schiff bases in an easy way.

Results and discussion

Ligand synthesis

All of the new asymmetrical ligands reported in this study have been prepared in an analogous manner as shown in Scheme 1; their trivial names and structures are given in Fig. 1. The synthesis of all ligands involves three common steps. The first step involves a conventional carbodiimide amide

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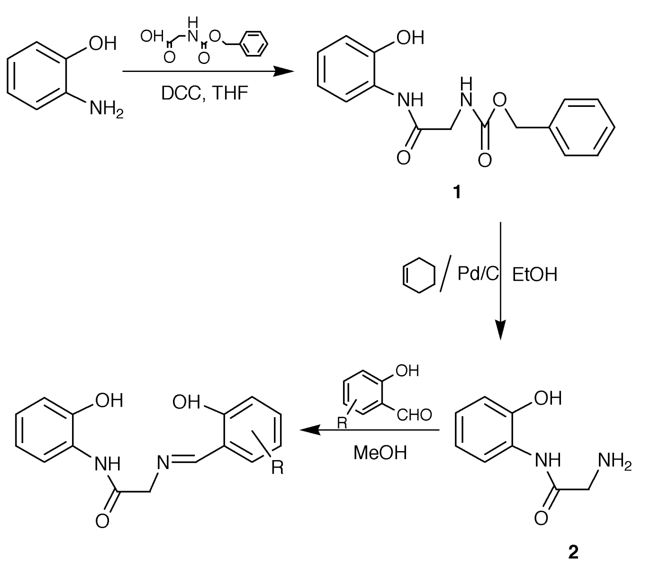
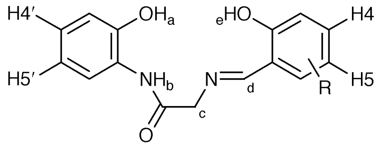


Scheme 1 Synthesis of the Schiff base ligands.

coupling[11] of carbobenzyloxyglycine with 2-hydroxyaniline in THF. As expected, this reaction proceeds in excellent yield (see Experimental) and large quantities of amide **1** can be readily prepared. There are many methods that have been reported for the removal of the Z protecting group from amine functionalities. We found the most convenient method to be *via* sacrificial hydrogenation using cyclohexene and palladium on charcoal as catalyst.[12] This methodology very rapidly yielded the desired amine **2** in high yield, without the need for any further purification. Amine **2** has then been employed as the precursor in the preparation of all of the new ligands *via* conventional Schiff base condensation reactions with commercially available salicylaldehydes. All of the new ligands have been satisfactorily characterised by elemental analysis ^{1}H, ^{13}C NMR and IR spectroscopies and mass spectrometry (see Experimental). We were keen to establish that the ligands were capable of acting as tetradentate ligands before embarking on a prelonged electrochemical synthesis programme. Therefore, we decided that it was worthwhile to attempt to crystallise one of the ligands to confirm that they are conformationally compatible with the necessary tetradentate co-ordination mode in an octahedral geometry.



Name	R
H_3-amsal	H
H_3-amsal-5Cl	5Cl
H_3-amsal-5Br	5Br
H_3-amsal-3OEt	3OEt
H_3-amsal-3OMe, 5Br	3OMe, 5Br
H_3-amsal-3,5Cl	3,5Cl
H_3-amsal-3,5Br	3,5Br
H_3-amsal-3Br, 5Cl	3Br, 5Cl
H_3-amsal-3Br, 5NO_2	3Br, 5NO_2

Fig. 1 Structures of the Schiff base ligands.

Crystal structure of H_3-amsal

Yellow plate-like crystals of H_3-amsal, suitable for single crystal X-ray diffraction studies, were obtained by slow evaporation of an ethanol solution of the ligand. The crystal structure, with the atomic numbering scheme, is shown in Fig. 2. Some selected bond lengths and angles, as well as potential hydrogen bonds and bonding scheme, are listed in Table 1.

The crystal structure reveals that H_3-amsal exists as discrete molecules. An intramolecular hydrogen bond exists between the imine nitrogen atom N(2) and the phenolic oxygen atom O(3) [O(3)···N(2) = 2.615(4) Å and N(2)···H(3a)–O(3) = 147.7(3)°]. These intramolecular hydrogen bonds are typical of Schiff bases derived from salicylaldehydes.[13]

An additional bifurcated interaction also occurs between the amido H atom H(1b) and O(1) and N(2), as indicated in Table 1. Significant intermolecular interactions *via* hydrogen bonds can also be observed between the phenolic oxygen atom O(1) of one molecule and the amido oxygen atom O(2′) of a neighbouring molecule [O(1)···O(2′) = 2.662(3) Å and O(2′)···H(1a)–O(1) = 177.7(3)°]. Additional interactions can

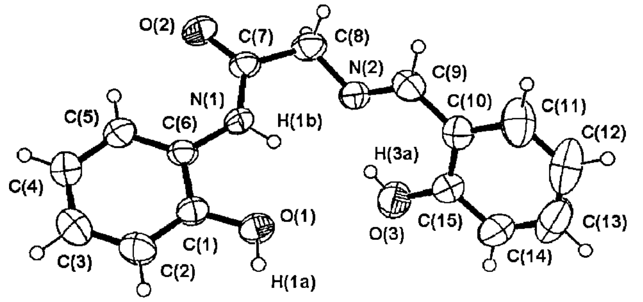


Fig. 2 ORTEP plot of H_3-amsal. Atoms showing the atomic numbering scheme are represented by their 40% probability ellipsoids.

Table 1 Selected bond lengths (Å) and angles (°) for the ligand H_3-amsal

N(1)–C(6)	1.414(3)	N(2)–C(8)	1.451(3)
N(1)–C(7)	1.342(3)	N(2)–C(9)	1.268(4)
O(1)–C(1)	1.367(3)	O(2)–C(7)	1.235(3)
O(3)–C(15)	1.355(4)		
N(1)–C(7)–C(8)	116.9(3)	C(1)–C(6)–N(1)	115.3(2)
C(7)–N(1)–C(6)	129.6(2)	C(9)–N(2)–C(8)	120.7(3)
N(2)–C(9)–C(10)	123.0(3)	N(2)–C(8)–C(7)	114.1(2)
O(1)–C(1)–C(2)	124.2(3)	O(1)–C(1)–C(6)	116.4(2)
O(2)–C(7)–N(1)	122.4(3)	O(2)–C(7)–C(8)	120.7(2)
O(3)–C(15)–C(14)	119.1(3)	O(3)–C(15)–C(10)	120.9(3)

Possible hydrogen bond scheme

D–H···A	D–H	H···A	D···A	D–H···A	H···A*···A′	Sum (XZ)
O(1)–H(1a)···O(2)$^{\neq 1\,a}$	0.820(3)	1.843(3)	2.662(3)	177.7(3)		
N(1)–H(1b)···O(1)	0.860(3)	2.189(3)	2.607(3)	109.6(2)		
N(1)–H(1b)···N(2)	0.860(3)	2.261(3)	2.713(3)	112.8(2)	137.56(15)	360.0(3)
O(3)–H(3a)···N(2)	0.820(5)	1.885(4)	2.615(4)	147.7(3)		
O(3)–H(3a)···O(3)$^{\neq 2\,a}$	0.820(5)	2.571(5)	2.980(5)	112.3(3)′	99.63(18)	359.6(5)

[a] Symmetry operations. $^{\neq 1}1/2 + x, 3/2 - y, -1/2 + z$; $^{\neq 2} - x, 1 - y, 2 - z$.

also exist between neighbouring phenolic atoms through H(3a).

Despite the mentioned intramolecular interactions and a partial conjugation of the molecule, it is not planar, probably due to the packing based on the intermolecular hydrogen bonds. Thus, the angle formed by the two potentially chelate planes [N(2)C(9)C(10)C(15)O(3) and O(1)C(1)C(6)N(1)] has a value of 61.6(3)°. If we consider that both amido and salycilaldehyde residues are rather planar, and that just a slight turn around the N(2)–C(8) bond can provide a rather planar spatial conformation, we can expect that this ligand should easily act as a tetradentate donor in the equatorial plane about an octahedral metal centre. Other bond lengths and angles are typical and merit no further discussion.[14–16]

Electrochemical synthesis of manganese complexes

In the light of the crystal structure of H_3-amsal it was clear that the series of ligands were potentially trianionic Schiff bases capable of co-ordinating in a tetradentate mode. We therefore instigated a synthetic programme in which a manganese anode was oxidised in an acetontitrile solution of the ligand in the presence of a small quantity of tetraethylammonium perchlorate as a supporting electrolyte.[17] It soon became apparent that the electrochemical oxidation of manganese in the presence of an acetonitrile solution of these ligands presents a simple and efficient route to neutral manganese(III) complexes of stoichiometry Mn^{III}(amsal-R)$(H_2O)_n$. This synthetic route allows the complexes to be isolated in high yields and with high purity. Thus, this is the most direct method we have found to obtain manganese(III) compounds and it clearly improves on the results obtained by using the Boucher procedure.

The electrochemical efficiency of the cell E_f was close to 0.33 mol F^{-1}, which is compatible with the following reaction scheme:

Cathode: H_3-amsal-R + 3 e^- → 3/2 $H_2(g)$ + amsal-R^{3-}

Anode: amsal-R^{3-} + Mn → Mn(amsal-R) + 3 e^-

The manganese complexes formed *via* this synthetic route are brown or greenish brown powdery solids, which all melt at over 300 °C. They are all obtained in high yields and are insoluble or sparingly soluble in water and common organic solvents, and quite soluble in polar aprotic co-ordinating solvents such as DMF and DMSO and appear to be stable in the solid state and in solution.

Elemental analyses (Table 2) of the complexes indicate that the manganese complexes have the general stoichiometry Mn(amsal-R)$(H_2O)_n$, suggesting that the complexes are neutral manganese(III) species in which the ligand is trideprotonated. This is supported by molar conductivity measurements for the complexes in 10^{-3} M DMF solutions, which are in the range 4.6–23.4 Ω^{-1} cm^2 mol^{-1}, indicating the non-electrolyte nature of the complexes,[18] which is completely consistent with this formulation.

All the fast atom bombardment (FAB) mass spectra show peaks (Table 2) relating to fragments of the form $[MnL]^+$, indicating ligand co-ordination to the metal centre. Furthermore, some complexes exhibit peaks due to the fragment $[Mn_2L_2]^+$, which could be tentatively attributed to the presence of dimeric species in the solid state.

All complexes exhibit very similar infrared spectral features. Bands centred at *ca.* 3400 cm^{-1} can be assigned to a combination of the ν(OH) modes of co-ordinated and lattice water. Strong bands attributable to ν(CN) are evident; these all show a shift of 3–48 cm^{-1} to lower energy from the free ligand values indicative of co-ordination to manganese. In addition, bands due to the amide I [ν(CO)] mode undergo positive shifts whereas the amide II [δ(NH) + ν(CN)] mode bands undergo negative shifts. This behaviour is compatible with the participation of the amide nitrogen atom in the co-ordination to the metal.[19]

The room temperature magnetic susceptibility data (in Table 2) for these compounds is also consistent with the formulation of the complexes as Mn(amsal-R)$(H_2O)_n$. All of the complexes exhibit room temperature magnetic moments close to the spin-only value of 4.9 μ_B expected for a magnetically dilute octahedral high-spin d^4 manganese(III) ion. The magnetic behaviour has been studied in the temperature range 50–300 K and all complexes are found to obey the Curie–Weiss law. This study shows little or no antiferromagnetic interaction between close metal centres in the solid state. An example is shown in Fig. 3 for the complex Mn(amsal)(H_2O). The conclusion that can be drawn from these magnetic data is that it is unlikely that there are strong associations between manganese centres, implying that the complexes exist as either monomers or as very weakly associated oligomers or polymers.[20] Unfortunately, our extensive efforts to obtain crystals suitable for single crystal X-ray diffraction studies, in order to

Table 2 Analytical and other data for the complexes

Complex	Analysis/%[a] C	Analysis/%[a] H	N	FAB[b] *m/z*	μ_{eff}/μ_B	Redox potentials[c] E_{ox}/V	Redox potentials[c] E_{red}/V
Mn(amsal)(H_2O)	52.7(52.8)	4.2(4.0)	8.6(8.2)	323.0	4.7	0.782 —	— −0.658
Mn(amsal-5Cl)(H_2O)	48.1(47.9)	3.3(3.5)	7.5(7.5)	357.5	5.1	0.812 —	— −0.622
Mn(amsal-5Br)$(H_2O)_{1.5}$	41.5(42.0)	3.0(3.3)	6.4(6.5)	401.9(804.7)*	5.1	0.794 −0.440	— −0.600
Mn(amsal-3OEt)$(H_2O)_4$	46.2(46.6)	5.0(4.7)	6.3(6.4)	349.9	5.3	0.760 —	— −0.748
Mn(amsal-3OMe,5Br)$(H_2O)_3$	39.5(39.6)	3.5(3.7)	6.0(5.8)	431.9(862.8)*	5.1	0.768 −0.432	— −0.600
Mn(amsal-3,5Cl)(H_2O)	44.2(44.0)	3.0(2.7)	7.3(6.9)	390.0	5.3	0.820 —	— −0.730
Mn(amsal-3,5Br)$(H_2O)_2$	34.9(34.9)	2.1(2.5)	5.6(5.4)	479.8(959.6)*	5.3	0.802 —	— −0.502
Mn(amsal-3Br,5Cl)(H_2O)	39.5(39.7)	2.7(2.4)	6.5(6.2)	436.6	5.0	0.810 —	— −0.664
Mn(amsal-3Br,5NO_2)$(H_2O)_2$	36.9(37.4)	2.3(2.7)	8.9(8.7)	447.0	5.2	0.782 −0.664	— −0.804

[a] Found (calculated). [b] Peaks correspond to $[MnL]^+$ except those marked with a *, which correspond to $[Mn_2L_2]^+$. [c] Potentials *vs.* SCE.

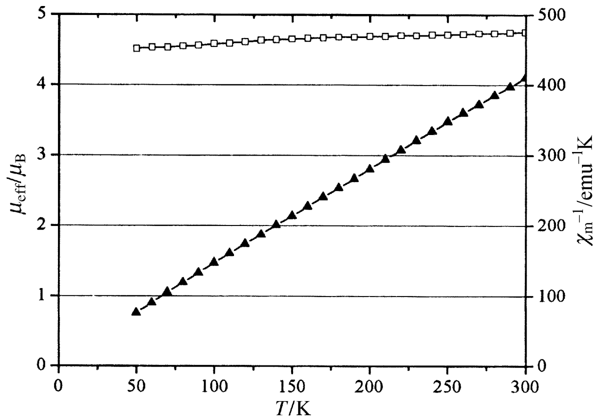


Fig. 3 Plots of μ_{eff} (□) and $1/\chi_M$ (▲) *vs.* temperature for $Mn(amsal)(H_2O)$.

establish the structural make-up of these complexes, have been unsuccessful. Thus, we decided to investigate whether paramagnetic ^1H NMR of the complexes in solution could be of utility in assigning their structures further.

Table 3 ^1H NMR data for the complexes

Complex	H4	H5	H4′	H5′
$Mn(amsal)(H_2O)$	−36.6	−26.2	−18.5	−17.3
$Mn(amsal\text{-}5Cl)(H_2O)$	−37.7	na[a]	−22.3	−17.5
$Mn(amsal\text{-}5Br)(H_2O)_{1.5}$	−37.7	na	−22.2	−17.5
$Mn(amsal\text{-}3OMe,5Br)(H_2O)_3$	−37.5	na	−23.7	−18.0

[a] na, not applicable.

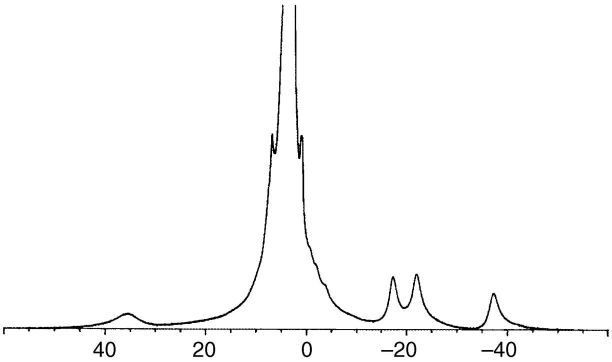


Fig. 4 ^1H NMR spectrum for the complex $Mn(amsal\text{-}5Br)(H_2O)_{1.5}$.

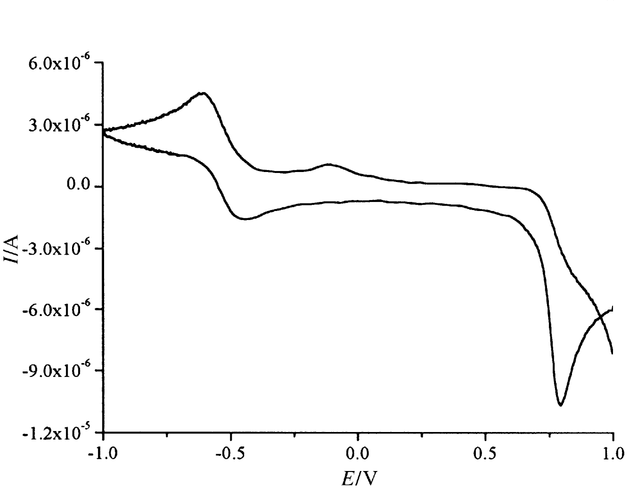


Fig. 5 Cyclic voltammogram for $Mn(amsal\text{-}5Br)(H_2O)_{1.5}$ at scan rate of 0.02 V s^{-1}.

^{1}H NMR studies

Our findings for these complexes are broadly consistent with those of Pecoraro and co-workers[21] and also with our own results[22,23] for Mn(III) complexes with related Schiff bases. These data are presented in Table 3. The protons *ortho* to the donor atoms of the Schiff base ligand, H3, H3′, H6 and H6′ (see Fig. 1) are not observed. Three or four resonances are observed between −17.1 and −37.7 ppm, which we have assigned, in accordance with Pecoraro's observations and other studies done by us,[22,23] to the H4 and H5 protons of the aldehyde and to H4′ and H5′ protons of the amine (see Fig. 4). Most interestingly, we observe a resonance at +36 ppm, which we can assign to the aliphatic protons in the methylene bridge between the imine and amide nitrogen atoms. This is in contrast to both our previous studies and those of Pecoraro and co-workers. To the best of our knowledge, no signals of a methylene group adjacent to an atom co-ordinated to the manganese(III) centre have previously been observed. These data serve to substantiate the formation of manganese(III) complexes, but they do not enable any further deductions to be made as to the structural make-up of the complexes or of any solution behaviour.

Cyclic voltammetry studies

Since one of the main driving forces behind this study was to ascertain whether it was possible to stabilise higher oxidation states of manganese with these ligands it was necessary to investigate the electrochemical behaviour of the complexes. Cyclic voltammograms of all of the complexes were obtained as 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 2 and a typical voltammogram is shown in Fig. 5.

In general all voltammograms show an irreversible oxidative process between 0.760 and 0.820 V, which we assign to the oxidation of manganese(III) to manganese(IV). It is interesting to note that the potentials of these processes are similar to those found in manganese(III) complexes with the Schiff base salpn and oxyanions.[24] In the latter case, the stabilisation of the manganese(IV) oxidation level is basically due to the presence of one additional basic oxyanion per manganese, which provides another negative charge to the Mn ion. In our complexes we do not have an additional basic ligand, but the presence of the amide nitrogen atoms must be responsible for the easy stabilisation of the Mn(IV) in these systems.

A second redox wave, assigned to the Mn(II)↔Mn(III) process, is observed at negative potentials. Most of the complexes suffer an irreversible reductive process [Mn(III) → Mn(II)] but some of them (see Table 2) present an important rate of reversibility.

In all cases the most significant wave is that corresponding to the oxidation of manganese(III) to manganese(IV), suggesting that the ligands readily stabilise higher oxidation states of manganese, as previously found for ligands with amido groups.[9,10,25,26]

Conclusion

A high yielding route to a new class of potentially trianionic and tetradentate asymmetrical Schiff base ligands has been developed. We have shown that the presence of an amido donor in the asymmetrical ligand results in the easy oxidation of a manganese anode in the presence of an acetonitrile solution of the ligands to manganese(III) rather than manganese(II). It thus provides a new and simple way to prepare neutral manganese(III) complexes. The structural characterisation of the complexes indicates an octahedral environment around the metal centre.[27] Finally, cyclic voltammetry suggests that these complexes can be readily oxidised and that they could

Table 4 Elemental analyses, mass spectrometry and melting points for the ligands

Ligand	Analysis/%[a] C	H	N	MS-EI *m*/*z*	Mp/°C
H_3-amsal	66.2(66.7)	5.2(5.2)	10.4(10.4)	270.2	181
H_3-amsal-5Cl	59.0(59.1)	4.4(4.3)	9.3(9.2)	304.0	180
H_3-amsal-5Br	51.3(51.6)	3.3(3.7)	8.0(8.0)	348.0	181
H_3-amsal-3OEt	64.7(64.9)	5.9(5.7)	8.4(8.9)	314.1	180
H_3-amsal-3OMe,5Br	50.7(50.7)	3.7(4.0)	7.7(7.4)	378.0	184
H_3-amsal-3,5Cl	52.7(53.1)	3.3(3.5)	8.4(8.3)	338.0	192
H_3-amsal-3,5Br	41.8(42.1)	2.7(2.8)	6.9(6.5)	427.8	199
H_3-amsal-3Br,5Cl	47.2(47.0)	3.1(3.1)	7.4(7.3)	384.0	189
H_3-amsal-3Br,$5NO_2$	44.5(44.7)	2.8(3.1)	10.9(10.7)	393.0	199

[a] Found (calculated).

act as precursors to other high-valent compounds of manganese. Investigations into chemical oxidation of these complexes are currently underway.

Experimental

Chemicals of the highest commercial grade available (Aldrich) were used as received. Manganese metal (Ega Chemie) was used as platelets and was cleaned of oxide in dilute hydrochloric acid prior to electrolysis.

Physical measurements

Elemental analyses were performed on a Carlo Erba EA 1108 analyser. The NMR spectra were recorded on a Bruker WM-250 spectrometer using DMSO-d_6 as solvent. Infrared spectra were recorded as KBr pellets on a Bio-Rad FTS 135 spectrophotometer in the range 4000–600 cm^{-1}. 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 a matrix. Magnetic susceptibility measurements in the 50–300 K temperature range were obtained 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 °C from 10^{-3} M solutions in DMF on a WTW model LF-3 instrument. Cyclic voltammetry was performed on an EG&G PAR model 273 potentiostat, controlled by 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.

Schiff base ligand preparation

Ligands were prepared according to a method in three steps as shown in Scheme 1.

Synthesis of *N*-(2-hydroxyphenyl)-2-[(phenylmethoxy)-carbonylamino]ethanamide (1). To a solution of carbobenzyloxyglycine (5.00 g, 23.90 mmol) in THF (100 cm^3) were added 2-hydroxyaniline (2.61 g, 23.90 mmol) and a slight excess of *N*,*N*′-dicyclohexylcarbodiimide (5.30 g, 25.69 mmol). This mixture was stirred at room temperature for 4 h. The insoluble *N*,*N*′-dicyclohexylurea was removed by filtration and the solvent replaced by ethyl acetate (100 cm^3). The addition of petroleum ether 40–60 °C afforded 6.46 g (90%) of the amine **1**. (Found: C, 64.1; H, 5.5; N, 9.4. Calcd. for $C_{16}H_{16}N_2O_4$: C, 64.0; H, 5.4; N, 9.3). ^1H NMR (DMSO-d_6): δ 4.06 (d, 2H), 5.30 (s, 2H), 6.96 (m, 1H), 7.56 (m, 5H), 7.91 (t, 1H), 8.09 (d, 1H), 9.31 (s, 1 H), 10.09 (s, 1 H). ^{13}C NMR (DMSO-d_6): δ 44.7 (CH_2–NH), 65.9 (O–CH_2), 115.6–147.5 (C_{arom}), 157.0 (HN–CO–O), 168.4 (HN–CO). IR (KBr, cm^{-1}): ν(OH) 3392 (s), ν(NH) 3270 and 3075 (s), ν(amide I) 1677 (vs), ν(amide II) 1618 (s). Mp: 172 °C. Mass spectrometry (EI): *m*/*z* 300.1.

Synthesis of 2-amino-*N*-(2-hydroxyphenyl)ethanamide (2). A solution of **1** (2.00 g, 6.70 mmol) in ethanol (100 cm^3) was mixed with cyclohexene (5 cm^3, in excess to the molar proportion required) and 0.50 g of a commercial 10% Pd–C catalyst (catalyst:susbstrate ratio 1 : 4 by weight).[12] The mixture was

Table 5 ^1H and ^{13}C NMR data for the ligands in DMSO-d_6

Ligand	^1H NMR[a] a	b	c	d	e	H_{arom}	R	^{13}C NMR CH_2	C_{arom}	CN	CO	R
H_3-amsal	10.14(br)	9.47(s)	4.68(s)	8.80(s)	12.90(br)	6.91–8.12		62.0	115.8–160.4	167.5	168.2	
H_3-amsal-5Cl	9.99(br)	9.34(s)	4.51(s)	8.62(s)	12.58(br)	6.80–7.95		59.0	115.8–157.9	165.8	167.4	
H_3-amsal-5Br	9.95(br)	9.38(s)	4.53(s)	8.63(s)	12.63(br)	6.89–7.96		60.0	115.8–158.8	166.3	168.0	
H_3-amsal-3OEt	9.95(br)	9.31(s)	4.52(s)	8.63(s)	12.78(br)	6.75–7.95	4.06(q) OCH_2 1.33(t) CH_3	57.4	115.7–150.2	166.0	168.5	66.0 OCH_2 15.4 CH_3
H_3-amsal-3OMe,5Br	9.97(br)	9.35(s)	4.51(s)	8.58(s)	—	6.77–7.91	3.82(s) CH_3	58.1	115.7–153.5	166.2	168.3	58.4 CH_3
H_3-amsal-3,5Cl	9.97(br)	9.48(s)	4.67(s)	8.60(s)	14.29(br)	6.83–7.87		59.6	115.9–161.5	165.5	167.9	
H_3-amsal-3,5Br	9.91(br)	9.55(s)	4.65(s)	8.60(s)	14.44(br)	6.82–7.85		59.6	115.9–163.2	166.4	168.6	
H_3-amsal-3Br,5Cl	9.88(br)	9.50(s)	4.67(s)	8.59(s)	14.40(br)	6.85–7.87		57.9	115.8–162.1	164.5	168.3	
H_3-amsal-3Br,$5NO_2$	9.88(s)	9.68(s)	4.72(s)	8.80(s)	13.57(br)	6.79–8.49		58.0	115.9–169.2	166.6	168.5	

[a] See Fig. 1 for atom labelling

Table 6 Selected IR bands (in cm^{-1}) for the ligands[a]

Ligand	ν(OH)	ν(NH)	ν(amideI)	ν(CN)	ν(amideII)
H_3-amsal	3379s	3072s,br	1656vs	1635vs	1615m
H_3-amsal-5Cl	3393s	3072s,br	1656vs	1636vs	1616s
H_3-amsal-5Br	3398s	3068s,br	1661vs	1633vs	1616vs
H_3-amsal-3OEt	3312m	3091s,br	1650vs	1624s	1595m
H_3-amsal-3OMe,5Br	3435m	3045m	1662s	1649vs	1598m
H_3-amsal-3,5Cl	3404s	3071m	1695vs	1662vs	1612m
H_3-amsal-3,5Br	3406m	3063m	1693s	1660vs	1615s
H_3-amsal-3Br,5Cl	3407m	—	1694s	1662vs	1614m
H_3-amsal-3Br,5NO_2	3406m	3098m	1693s	1664vs	1604s

[a] Intensities are denoted by: vs very strong, s strong, m medium, br broad.

Table 7 Experimental conditions for the electrochemical synthesis (initial current 10.0 mA)

Compound	Time/h	Initial voltage/V	Am of Mn dissolved/mg	E_f [a]/mol F^{-1}
Mn(amsal)(H_2O)	5.9	12.0	39.5	0.33
Mn(amsal-5Cl)(H_2O)	5.3	9.6	42.3	0.39
Mn(amsal-5Br)$(H_2O)_{1.5}$	4.6	13.7	40.0	0.42
Mn(amsal-3OEt)$(H_2O)_4$	5.1	32.1	33.8	0.32
Mn(amsal-3OMe,5Br)$(H_2O)_3$	4.2	9.3	25.6	0.41
Mn(amsal-3,5Cl)(H_2O)	4.7	22.0	31.1	0.32
Mn(amsal-3,5Br)$(H_2O)_2$	3.8	9.2	29.3	0.38
Mn(amsal-3Br,5Cl)(H_2O)	4.2	15.0	28.3	0.33
Mn(amsal-3Br,5NO_2)$(H_2O)_2$	4.1	42.7	27.6	0.33

[a] Electrochemical efficiency of the cell, defined as the amount of metal dissolved per Faraday of charge.

refluxed for 15 min, filtered from catalyst, the catalyst washed with ethanol, and the combined filtrates evaporated under reduced pressure to give the deprotected amine **2** (yield 1.05 g, 95%). (Found: C, 57.5; H, 6.2; N, 16.6. Calcd. for $C_8H_{10}N_2O_2$: C, 57.8; H, 6.1; N, 16.9). ^1H NMR (DMSO-d_6): δ 3.26 (s, 2 H), 6.77 (m, 1H), 6.88 (s, 1H), 6.89 (s, 1H), 8.18 (d, 1H). ^{13}C NMR (DMSO-d_6): δ 45.2 (CH_2), 114.9–146.6 (C_{arom}), 171.5 (CO). IR (KBr, cm^{-1}): ν(OH) 3431 (s), ν(NH_2) 3420 and 3252 (s), ν(NH) 3083 (s, br), ν(amide I) 1649 (vs), ν(amide II) 1614 (s). Mp: 148 °C. Mass spectrometry (EI): *m/z* 166.0.

Preparation of Schiff base ligands. All of the Schiff base ligands were prepared in a standard manner by the reaction of equimolecular quantities of the appropriate aldehyde and amine **2**, which is typified by the preparation of H_3-amsal. The amine **2** (1.25 g, 7.53 mmol) and salicylaldehyde (0.80 cm^3, 7.53 mmol) were dissolved in methanol (100 cm^3) and the solution was brought to reflux. The volume of the solution was reduced over a 3 h period to *ca.* 50 cm^3, using a Dean–Stark trap, and was then allowed to cool. The solid, which precipitated, was collected by filtration, washed with diethyl ether (3 cm^3) and dried *in vacuo*. The purity of all ligands was checked by elemental analysis (Table 4), ^1H and ^{13}C NMR (Table 5), IR (Table 6) spectroscopy and mass spectrometry (Table 4).

Synthesis of the complexes

The compounds were all obtained using a standard electrochemical procedure as previously reported.[28,17] The conditions are given in Table 7. An acetonitrile solution of the Schiff base ligand containing tetraethylammonium perchlorate, as supporting electrolyte, was electrolysed using a platinum wire as the cathode and a manganese platelet as the anode. The cell can be summarised as: Pt(−)|(H_3-amsal-R) + MeCN|Mn(+).

The synthesis is typified by the preparation of Mn(amsal-3,5Br)$(H_2O)_2$: a suspension (0.2 g, 0.47 mmol) of the ligand in acetonitrile (80 cm^3), containing 20 mg of tetraethylammonium perchlorate, was electrolysed for 3.8 h using a current of 10 mA. During the electrolysis, nitrogen was bubbled through the solution to ensure the presence of an inert atmosphere. The brown solid obtained was washed with diethyl ether and dried *in vacuo*.

Crystallographic measurements. Crystal data and refinement details are given in Table 8. Plate-like yellow crystals of H_3-amsal were obtained by recrystallisation of the ligand from ethanol. Data were collected using a Siemens SMART diffractometer employing graphite-monochromated Mo-Kα (λ = 0.710 73 Å) radiation using ω scans ($2\theta_{max}$ = 50.08°). The structure was solved by direct methods[29] and refined by full matrix least squares on F^2.[30] An absorption correction was applied.[31] All non-hydrogen atoms were refined anisotropically and hydrogen atoms were included in calculated positions using a riding model.

Table 8 Crystal data and details of refinement for ligand H_3-amsal

Formula	$C_{15}H_{14}N_2O_3$
M	270.28
Crystal system	Monoclinic
Space group	$P2_1/n$
a/Å	6.6655(2)
b/Å	16.4067(5)
c/Å	12.793 80(10)
β/°	94.307(2)°
U/Å^3	1395.16(6)
T/K	298(2)
Z	4
μ/mm^{-1}	0.091
Reflections collected	2982
No. unique reflections	2451 (R_{int} = 0.0524)
R	0.0584
R′	0.1288

CCDC reference number 440/170. See http://www.rsc.org/suppdata/nj/b0/b000235f/ for crystallographic files in .cif format.

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