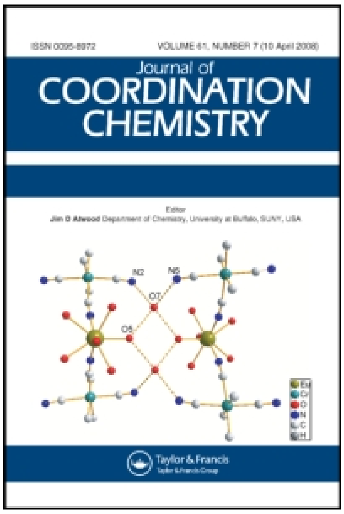

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A HIGH YIELD ROUTE TO NOVEL MANGANESE(III) COMPLEXES

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A HIGH YIELD ROUTE TO NOVEL MANGANESE(III) COMPLEXES

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Neutral manganese(III) complexes have been prepared, with high yield and purity, by a modification of the Boucher synthesis, using asymmetrical Schiff base ligands. These ligands [H_3-amsal = 3-aza-4-(2-hydroxyphenyl)-*N*-(2-hydroxyphenyl)but-3-enamide], incorporating hard donor atoms, are derived from the condensation of an amine precursor containing an amide group and substituted salicylaldehydes. The complexes are found to be of the form Mn^{III} (amsal-*R*)$(H_2O)_n$ ($n = 0.5, 3$) and have been characterised by various methods. Data point to octahedral geometry at the manganese atom.

Keywords: Manganese; Schiff bases; Amides; Cyclic voltammetry; Paramagnetic ^1H NMR

INTRODUCTION

Interest in the coordination chemistry of manganese complexes in high oxidation states is largely driven by the desire to prepare functional models of manganese-containing biological systems, such as superoxide dismutases [1], azide-insensitive catalases [2, 3], and other peroxidases [4]. In addition, catalytic properties of manganese complexes in different organic processes, *e.g.*, in the epoxidation of olefins [5], make this research area attractive. In order to develop this coordination chemistry we are trying to design new ligands able to resist the oxidising power of manganese ions in high oxidation states.

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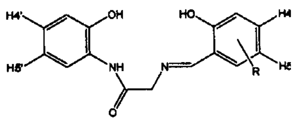
*Corresponding author.



Ligand	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

FIGURE 1 Structure of the ligands H_3-amsal-*R*.

For a long time the widely used method for the synthesis of manganese(III) complexes was the Boucher synthesis [6]. A modification of this method has been used in the isolation of manganese(III) complexes with symmetrical and asymmetrical Schiff base ligands [7–14]. Although we obtained interesting results, the yields were not good and the compounds not usually very pure.

In recent papers we have described a direct route to obtain manganese(III) complexes using a new class of asymmetrical ligands [15]. We have found that electrochemical synthesis is a very convenient route to prepare neutral manganese(III) complexes with ligands containing amide groups.

As an extension of all these studies we were interested in checking the behaviour of these Schiff bases containing amide groups in order to prepare high oxidation state manganese complexes. Herein we report the stabilisation of manganese(III) complexes with new amide ligands (see Fig. 1) using a variation of the Boucher method.

EXPERIMENTAL

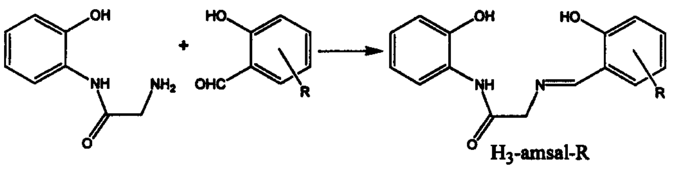
All reagents and solvents were used as received, without further purification. Elemental analyses were performed on a Carlo Erba EA 1108 instrument. NMR spectra were recorded on a Bruker WM-250 spectrometer using DMSO-d_6 as solvent. Infrared spectra as KBr pellets were recorded on a Bio-Rad FTS 135 spectrophotometer in the range 4000–600 cm^{-1}. Mass spectrometry was performed on a Hewlett Packard 5988A mass spectrometer using electron impact (EI), and fast atom bombardment (FAB) on a Micromass AutoSpec mass spectrometer, employing *m*-nitrobenzyl alcohol as matrix. Room temperature magnetic susceptibilities were measured on a Digital Measurement system (MSB-MKI), calibrated against tetrakis (isothiocyanato)cobaltate(II). Conductivities were measured at 25°C for 10^{-3} M solutions in DMF on a WTW model LF-3 instrument. Cyclic voltammetry was performed on an EG and G PAR model 273 potentiostat, controlled by EG and G PAR model 270 software, in conjunction with a three-electrode cell, fitted with 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 for ca. 10^{-3} M dimethylformamide solutions of the metal complexes containing 0.1 M tetraethylammonium perchlorate as supporting electrolyte.

Ligand Preparation

The ligands were prepared by the condensation of an amine precursor with an amide group and substituted salicylaldehydes (see Scheme 1), according to the general method previously proposed [15a]. They were satisfactorily characterised by ^{1}H and ^{13}C MMR, IR spectroscopy, mass spectrometry, and elemental analyses. One of them (H_3-amsal) was crystallographically characterised [15a]. This general synthesis is typified by the preparation of H_3-amsal.

H_3-amsal

2-amino-*N*-(2-hydroxyphenyl)ethanamide (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 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 the mixture was then allowed to cool. The solid, which precipitated, was collected by filtration,



SCHEME 1 Synthetic scheme for the ligands.

washed with diethylether ($3\,cm^3$) and dried *in vacuo*. *Anal.* Calcd. for $C_{15}H_{14}N_2O_3$ (%): C, 66.7; H, 5.2; N, 10.4. Found: C, 66.2; H, 5.2; N, 10.4. ^{1}H NMR (DMSO-d_6): δ4.68 (s, 2H, C—H_2), 6.91 – 8.12 (8 aromatic H), 8.80 (s, 1H, H—C=N), 9.47 (s, 1H, N—H), 10.14 (s, br, 1H, O—H), 12.90 (s, br, 1H, O—H). ^{13}C NMR (DMSO-d_6): δ 62.0 (CH_2), 115.8 – 160.4 (Carom), 167.5 (CN), 168.2 (CO). IR (KBr, cm^{-1}): ν(O—H) 3379 (s), ν(N—H) 3072 (s, br), ν(amide I) 1656 (vs), ν(C=N) 1635 (vs), ν(amide II) 1615 (m). Melting point: 181°C. EI-MS (M^+): 270.2 *m/z*.

Complex Preparation

All complexes were prepared following a variation of the Boucher method [6]. The synthesis is typified by the preparation of Mn(amsal)$(H_2O)_{0.5}$.

Mn(amsal)$(H_2O)_{0.5}$

To a suspension of the Schiff base ligand, H_3-amsal, (0.30 g, 1.10 mmol) in methanol : ethanol (1 : 1, $40\,cm^3$) was added $3\,cm^3$ of an aqueous solution of NaOH (0.13 g, 3.30 mmol). After 5 minutes stirring, a yellow solution was obtained. Then 0.43 g (1.18 mmol) of manganese(II) perchlorate hexahydrate in $10\,cm^3$ of methanol was added; a fast change of solution colour was observed, from yellow to brown passing through green (*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 in the presence of air for 12 h, the solid formed was collected by filtration, washed with diethylether and dried *in vacuo*.

RESULTS AND DISCUSSION

All complexes prepared are powders with low soluble in most common organic solvents, but are quite soluble in polar coordinating solvents such as DMF and DMSO. All melt over 300°C and appear to be air-stable in the solid state and in solution.

Elemental analyses were satisfactory and show that manganese(II) reacts with these Schiff base ligands to afford new solvated complexes of the form Mn(amsal-*R*)$(H_2O)_n$ ($n = 0.5, 3$) in high purity and almost quantitative yield. It is remarkable how the results achieved in this study compare with those usually obtained by the traditional Boucher method; this latter procedure usually yields ionic perchlorate complexes, while in the process reported herein perchlorate anion is not present and neutral complexes are obtained. Thus, it seems that these new ligands are capable, in a very simple way, of deprotonating easily in a basic medium, stabilising Mn(III) by oxidation of Mn(II) in solution and generating neutral Mn(III) complexes. In addition, all the complexes prepared by this method show a stoichiometry quite similar to those obtained using an electrochemical procedure [15a].

Infrared Spectroscopy

IR spectra of all the manganese(III) complexes are very similar, and confirm the lack of perchlorate anions. The most important frequencies are given in Table II. All complexes exhibit a very strong band at ca. 3400 cm^{-1}, indicative of the presence of coordinated and/or lattice water. Strong bands about 1630 cm^{-1}, characteristic of the ν(C=N) stretching mode, are shifted to lower frequencies from the free ligand values, indicating coordination of the ligand to the metal through the imine nitrogen atom. In most of the spectra the ν(C=N) band is overlapped with the amide I band and prevents its observation. When this band is observed, it is shifted to positive values from the free ligand. Moreover, bands due to the amide II [δ(NH) + ν(CN)] mode undergo negative shifts. This behaviour is compatible with the participation of the nitrogen amide atom in coordination to the metal [16].

FAB Mass Spectrometry

FAB mass spectrometry data for these complexes are given in Table I. All show peaks relating to fragments of the form $[MnL]^+$ indicating ligand coordination to the metal centre. Furthermore, some complexes exhibit peaks due to the fragment $[Mn_2L_2]^+$ which could be attributed to the presence of dimers in the solid state.

Magnetic Measurements

Room-temperature magnetic moments were corrected for diamagnetism of the sample using Pascal constants. Values obtained are shown in Table I. In all cases the results are close to 4.9 μ_β, typical for octahedral, high spin manganese(III) complexes prepared with symmetrical and asymmetrical Schiff base ligands [7–15, 17].

TABLE I Characteristic data for the complexes

Compound	*Colour*	*FAB*[a]*/m/z*	μ_{eff}/μ_B	*Redox potentials*[c] E_{ox} *(V)*	E_{red} *(V)*
Mn(amsal)$(H_2O)_{0.5}$	greenish brown	322.1 (645.0)[b]	5.1	0.788	−0.776
Mn(amsal-5Cl)$(H_2O)_{0.5}$	brown	356.1	5.0	0.768 −0.476	−0.646
Mn(amsal-5Br)$(H_2O)_{0.5}$	brown	401.1	5.1	0.760 −0.468	−0.654
Mn(amsal-3OEt)$(H_2O)_3$	dark brown	366.1	5.0	0.742	−0.700
Mn(amsal-3OMe,5Br)$(H_2O)_{0.5}$	reddish brown	440.0	5.1	0.736	−0.624
Mn(amsal-3,5Cl)$(H_2O)_{0.5}$	brown	391.1 (783.1)[b]	4.9	0.776 −0.412	−0.564
Mn(amsal-3,5Br)$(H_2O)_{0.5}$	pale brown	482.3	5.0	0.776 −0.422	−0.562
Mn(amsal-3Br,5Cl)$(H_2O)_{0.5}$	pale brown	436.0	5.1	0.778 −0.428	−0.548

[a] Peaks correspond to $[MnL]^+$ except those marked with.
[b] Which correspond to $[Mn_2L_2]^+$.
[c] Potentials *vs.* SCE.

TABLE II Most significant IR data (cm^{-1}) for the complexes

Compound	ν*(amide* I)	$\nu(C{=}N)$	ν*(amide* II)
Mn(amsal)$(H_2O)_{0.5}$	(1656 vs)*	1633 vs (1637 vs)	1595 sh (1615 m)
Mn(amsal-5Cl)$(H_2O)_{0.5}$	(1656 vs)	1638 s (1641 vs)	1592 m (1616 s)
Mn(amsal-5Br)$(H_2O)_{0.5}$	(1661 vs)	1637 vs (1643 vs)	1600 m (1616 vs)
Mn(amsal-3OEt)$(H_2O)_3$	1682 m (1650 vs)	1624 s (1627s)	1598 vs (1595 m)
Mn(amsal-3OMe,5Br)$(H_2O)_{0.5}$	1680 br (1662 s)	1630 vs (1649 vs)	1594 s (1598 m)
Mn(amsal-3,5Cl)$(H_2O)_{0.5}$	(1695 vs)	1631 vs (1662 vs)	1598 vs (1612 m)
Mn(amsal-3,5Br)$(H_2O)_{0.5}$	(1693 s)	1633 vs (1660 vs)	1600 s (1615 s)
Mn(amsal-3Br,5Cl)$(H_2O)_{0.5}$	(1694 s)	1630 vs (1662 vs)	1595 s (1614 m)

* Bands corresponding to the free ligands in parentheses; vs, very strong, s, strong, m, medium and sh, shoulder.

Conductivity Measurements

The measurement of molar conductivities was possible in DMF, and the obtained Λ_M values are in the range $4-13\,\Omega^{-1}cm^2mol^{-1}$, indicating the non-electrolyte nature of the compounds [18].

^{1}H NMR Studies

^{1}H NMR studies were undertaken for these complexes using DMSO-d_6 as a solvent. ^{1}H NMR shifts are listed in Table III, and in Figure 2 the paramagnetic ^{1}H NMR spectrum of the complex Mn(amsal)$(H_2O)_{0.5}$ is shown.

TABLE III ^1H NMR data for the complexes

Complex	H_4	H_5	$H_{4'}$	$H_{5'}$	$C—H_2$
$Mn(amsal)(H_2O)_{0.5}$	−36.7	−26.1	−18.3	−17.1	37.3
$Mn(amsal\text{-}5Cl)(H_2O)_{0.5}$	−37.8		−22.3	−17.6	35.2
$Mn(amsal\text{-}5Br)(H_2O)_{1.5}$	−37.5		−22.2	−17.5	35.9
$Mn(amsal\text{-}3OMe,5Br)(H_2O)_3$	−38.1		−24.6	−18.6	34.3

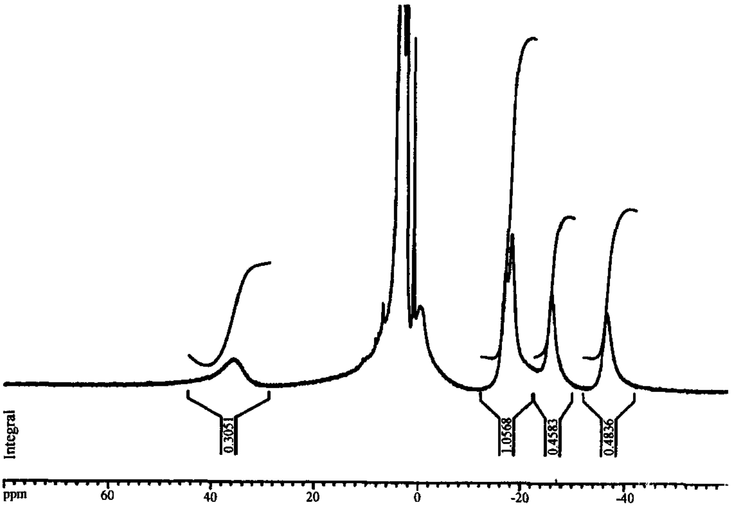


FIGURE 2 ^1H NMR spectrum for the complex $Mn(amsal)(H_2O)_{0.5}$.

The spectra contain four or five proton resonances that lie outside the diamagnetic region (ca. 0–10 ppm). This feature is the result of the spin delocalisation mechanism which gives rise to large chemical shifts for the phenolate protons [19]. Three or four signals are observed between −17.1 ppm and −38.1 ppm, which we have assigned to the 4, 5, 4′ and 5′ring protons (see Fig. 1) by using ring-substituted derivatives. These results are in accordance with Pecoraro's observations [20] and with previous findings for Mn(III) complexes with related Schiff base ligands [12, 15].

Most interestingly, we observe one broad peak downfield (~ +36 ppm) that we can assign to the aliphatic protons in the methylene bridge between the imine and amide nitrogen atoms. These data serve to substantiate the formation of manganese(III) complexes.

Cyclic Voltammetry Studies

Cyclic voltammograms of all complexes were obtained using dimethylformamide solutions at slow scan rates (0.02 V s^{-1}) over a potential range from

+1 to −1 V. Numerical data are given in Table I. In DMF solution most of the complexes exhibit similar behaviour. Their voltammograms show an irreversible oxidative process (**O2**) between 0.736 and 0.788 V which can be assigned to the oxidation of the metal centre from manganese(III) to manganese(IV). These values are lower than those found for Mn(III) complexes with similar Schiff base ligands which do not contain an amide group [9, 13, 17d]. On the other hand, these potentials are similar to those found in manganese(III) complexes with the Schiff base *salpn* and oxyanions [21]. In the latter case, the stabilisation of the manganese(IV) state is essentially due to the presence of one additional basic oxyanion per manganese. The present complexes are neutral and do not contain an additional basic ligand; thus the presence of the amide nitrogen atom must be responsible for the Mn(IV) stabilisation.

A second redox wave, assigned to the Mn(II) ↔ Mn(III) process, is observed at negative potentials. This process exhibits some reversibility, judging from the separation between the reduction (**R1**) and oxidation (**O1**) peaks. For three of these complexes (when $R = H$; 3OEt; 3OMe, 5Br) this process is irreversible. In all cases the peak corresponding to the oxidation of manganese(III) to manganese(IV) is the most intense and sharp wave in the voltammograms, suggesting that the ligands are able to stabilise high oxidation states of manganese, as previously found for ligands containing amide groups [15, 22, 23].

In summary, all the data obtained from the different characterisation techniques suggest octahedral geometry for these complexes. In this structure, the triply deprotonated Schiff base ligand would occupy the equatorial plane, bound to manganese(III) *via* imine and amide nitrogen and phenolic oxygen atoms. By analogy with other well-characterised complexes [12, 14, 17], the coordination sphere of the manganese centre could be completed by water or μ-phenoxy bridges between neighbouring units, generating monomeric or dimeric arrangements. $Mn^{III}L(H_2O)_n$ complexes are easily and readily obtained, in high purity and almost quantitative yield, by the modification of the Boucher method. As far as we know, these complexes are the first examples of neutral Mn(III) complexes obtained by this route. Previously, only complexes of the form $Mn^{II}L(H_2O)_n$ or $[Mn^{III}L(H_2O)_2]ClO_4 \cdot nH_2O$ were obtained.

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