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FULL PAPER

Mn(III) complexes with asymmetrical N_2O_3 Schiff bases. The unusual crystal structure of [Mn(phenglydisal-3-Br,5-Cl)(dmso)] (H_3phenglydisal = 3-aza-*N*-{2-[1-aza-2-(2-hydroxyphenyl)-vinyl]phenyl}-4-(2-hydroxyphenyl)but-3-enamide), a mononuclear single-stranded helical manganese(III) complex

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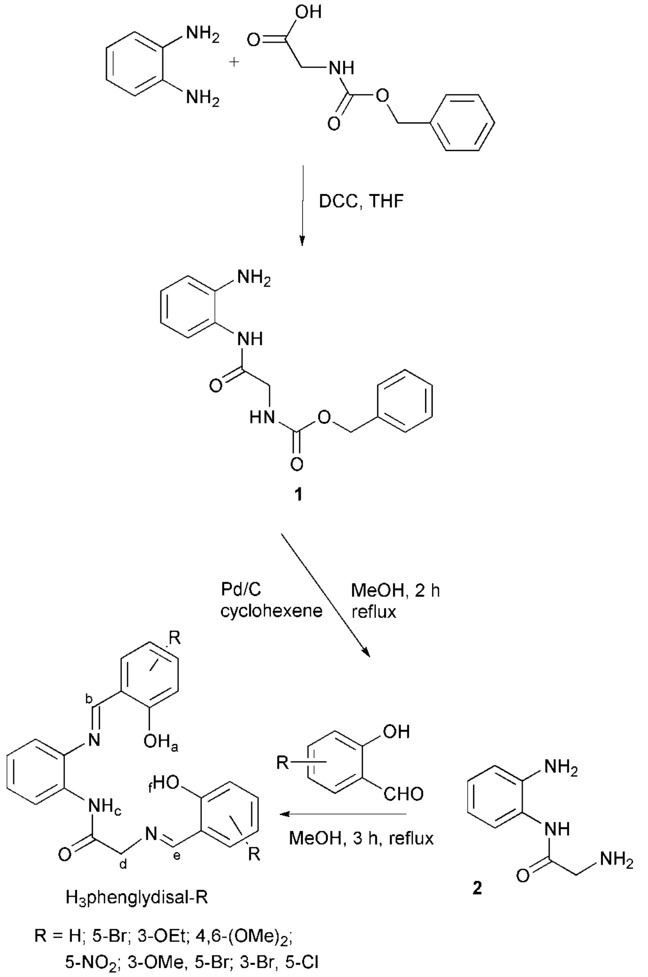
Neutral manganese(III) complexes, with potentially pentadentate and trianionic asymmetrical Schiff bases, containing a hard amido donor atom, have been synthesised. Complexes are found to be of the form Mn^{III}(phenglydisal-R)$(H_2O)_n$ (n = 1–4) [H_3phenglydisal = 3-aza-*N*-{2-[1-aza-2-(2-hydroxyphenyl)vinyl]phenyl}-4-(2-hydroxyphenyl)but-3-enamide; R = H; 3-OEt, 4,6-$(OMe)_2$, 5-NO_2, 3-OMe, 5-Br, 3-Br,5-Cl] and have been characterised by elemental analyses, FAB mass spectrometry, IR and ^1H NMR spectroscopies, magnetic measurements, molar conductivities and cyclic voltammetry. [Mn(phenglydisal-3-Br,5-Cl)(dmso)] **3**, was also crystallographically characterised and its crystal structure shows the manganese atom in an octahedral environment, with the ligand giving rise to a mononuclear single-stranded helical complex.

Introduction

There is current interest in the chemistry of high oxidation states of manganese, largely because of the occurrence of $Mn^{II/III/IV}$ states in biological sites such as the water oxidation centre of PSII[1–3] or the active centre of manganese catalase,[1,4] but also due to the formation of $Mn^{IV/V}$ intermediates in olefin oxidations or epoxidations catalysed by manganese complexes.[5]

As a continuation of our research activity on the co-ordination chemistry of manganese with Schiff bases,[6] we were interesting in designing new ligands capable of stabilising manganese in high oxidation states. Previous reports show that ligands containing amido donor groups form stable complexes with high valent transition metal ions.[7–9] Thus, as a beginning of this work, we prepared potentially tetradentate (N_2O_2) trianionic asymmetrical Schiff bases, which by an electrochemical method can yield neutral manganese(III) complexes.[10] The solution of the crystal structure of one of these ligands [3-aza-4-(2-hydroxyphenyl)-*N*-(2-hydroxyphenyl)but-3-enamide][10a] shows that the torsion angle between terminal aromatic rings is *ca.* 60°. In view of these results, we thought that growing the size of the ligand could maybe give rise to helical or even polynuclear species, so scarce in literature employing linear Schiff bases.[11] In fact, to the best of our knowledge, no helical Schiff base complexes containing manganese in a high oxidation state have been previously reported.

With these considerations in mind, the pentadentate (N_3O_2) trianionic asymmetrical Schiff bases shown in Scheme 1 were synthesised. We report the results achieved in their interaction with manganese(II) perchlorate by a modification of the Boucher method.[12]



Scheme 1 Reaction diagram for the isolation of H_3phenglydisal-R.

Results and discussion

Synthesis and characterisation of the ligands

The new asymmetrical ligands reported herein have all been

Table 1 Elemental analyses, mass spectrometry and melting points for the ligands

Ligand	Analysis[a] (%) C	H	N	MS-EI[b] m/z	Mp/°C
H_3phenglydisal-H	70.6 (70.8)	5.1 (5.1)	11.5 (11.3)	373.3	181
H_3phenglydisal-5-Br	48.7 (48.7)	3.0 (3.2)	7.8 (7.9)	531.9	205
H_3phenglydisal-3-OEt	67.6 (67.7)	6.0 (5.9)	9.2 (9.1)	461.2	183
H_3phenglydisal-4,6-$(OMe)_2$	63.0 (63.2)	5.3 (5.7)	8.2 (8.5)	493.2	184
H_3phenglydisal-5-NO_2	56.6 (57.0)	3.8 (3.7)	15.2 (15.1)	464.2	204
H_3phenglydisal-3-OMe,5-Br	48.3 (48.7)	3.4 (3.6)	7.1 (7.1)	592.1	201
H_3phenglydisal-3-Br,5-Cl	43.7 (44.0)	2.4 (2.5)	7.1 (7.0)	600.0	226

[a] Found (calculated). [b] Peaks corresponding to $[H_4L]^+$.

Table 2 Selected IR bands (in cm^{-1}) for the ligands[a]

Ligand	ν(OH)	ν(NH)	ν(amide I)	ν(CN)	ν(amide II)
H_3phenglydisal-H	3432m, br	3279m, br	1668vs	1616s	1640s
H_3phenglydisal-5-Br	3451m, br	3262m	1670vs	1615vs	1644m
H_3phenglydisal-3-OEt	3446w, br	3285m	1674 (sh)	1616m	1640m
H_3phenglydisal-4,6-$(OMe)_2$	3429m, br	3256m	1672 (sh)	1616 (sh)	1632vs
H_3phenglydisal-5-NO_2	3380m, br	3258w	1674 (sh)	1615vs	1658s
H_3phenglydisal-3-OMe,5-Br	3446m, br	3264m	1686 (sh)	1614m	1649vs
H_3phenglydisal-3-Br,5-Cl	3400m, br	3210m	1670m	1614s	1641s

[a] Intensities: vs = very strong, s = strong, br = broad, m = medium, w = weak, sh = shoulder.

Table 3 ^1H NMR data for the ligands in dmso-d_6[a]

Ligand	Proton a, f	b, e	c	d	H_{arom}	R	
H_3phenglydisal-H	12.20 (s) 12.10 (s)	8.65 (s) 8.52 (s)	8.47 (s)	4.60 (s)	6.45–7.40		
H_3phenglydisal-5-Br	12.80 (s) 12.40 (s)	8.89 (s) 8.56 (s)	9.78 (s)	4.50 (s)	6.78–8.0		
H_3phenglydisal-3-OEt	13.45 (s)	8.63 (s) 8.55 (s)	8.44 (s)	4.49 (s)	6.72–8.30	3.91 (q), 3.99 (q) 1.39 (t), 1.43 (t)	OCH_2 CH_3
H_3phenglydisal-4,6-$(OMe)_2$	12.36 (s) 12.47(s)	8.89 (s) 8.76 (s)	8.55 (s)	4.41 (s)	5.67–8.45	3.74 (s), 3.78 (s) 3.80 (s), 3.84 (s)	OCH_3
H_3phenglydisal-5-NO_2	14.00 (s)	9.05 (s) 8.80 (s)	9.95 (s)	4.65 (s)	6.65–8.70		
H_3phenglydisal-3-OMe,5-Br	13.05 (s) 12.56 (s)	8.90 (s) 8.50 (s)	9.79 (s)	4.50 (s)	7.00–7.80	3.90 (s) 3.80 (s)	OCH_3
H_3phenglydisal-3-Br,5-Cl	13.3 (s) 13.8 (s)	8.50 (s) 8.90 (s)	10.0 (s)	4.55 (s)	7.29–7.89		

[a] See Scheme 1 for atom labelling.

prepared in an analogous manner (Scheme 1). The synthesis of these ligands entails three common steps. The first step involves a conventional carbodiimide amide coupling[13] of carbobenzyloxyglycine with *o*-phenylenediamine in THF. As expected, this reaction proceeds in excellent yield (see Experimental section) and large quantities of amine **1** can be readily prepared. A second step implies the removal of the Z protecting group from the amine by sacrificial hydrogenation using cyclohexene and palladium on charcoal as catalyst.[14] This methodology quickly yields the desired amine **2** in high yield and with high purity. Amine **2** has been employed as the precursor in the preparation of the asymmetrical ligands *via* conventional condensation reactions with different commercially available salicylaldehydes. The obtained Schiff bases have been satisfactorily characterised by elemental analysis, mass spectrometry (Table 1), IR (Table 2) and ^1H NMR (Table 3) spectroscopies.

Mass spectrometry, IR and ^1H NMR spectroscopies

The mass spectra of the ligands show in all cases fragments of H_4L^+ of 100% intensity (see Table 1), in accord with the proposed formulae.

The most significant IR bands for the ligands are recorded in Table 2. They have been assigned by comparison with the IR spectrum of the amine precursor (see Experimental section) and on the basis of our knowledge in this field.

The ^1H NMR data for the ligands are shown in Table 3. The spectra of H_3phenglydisal-R, recorded using dmso-d_6 as solvent, exhibit two singlets between δ 8.5 and 9.1, assigned to the imine hydrogen atoms, corroborating the formation of C=N bonds. The aromatic protons lie in the range δ 5.6–8.7, while the presence of a singlet at δ *ca.* 4.5 indicates the presence of the methylene chain. Furthermore, all spectra show three singlets in the region of δ 8.4–13.8 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, which for H_3phenglydisal-3-OEt appears as an unique broad signal. This latter ligand also shows two quartets at δ *ca.* 3.9 and two triplets at δ *ca.* 1.4 indicating the presence of two non-equivalent ethoxy groups. The Schiff bases with methoxy substituents also show two or four singlets in the range δ 3.7–3.9.

Table 4 Analytical and other selected data for the complexes

Complex	Analysis[a] (%) C	H	N	FAB[b] *m*/*z*	μ_{eff}/μ_B
Mn(phenglydisal)(H_2O)$_4$	52.8(53.1)	4.9(4.9)	8.3(8.5)	426	5.1
Mn(phenglydisal-5-Br)(H_2O)$_2$	40.5(40.3)	3.2(3.4)	6.8(6.4)	582–583	5.2
Mn(phenglydisal-3-OEt)(H_2O)$_3$	54.6(55.0)	5.1(5.3)	7.1(7.4)	555	4.9
Mn{phenglydisal-4,6-(OMe)$_2$}(H_2O)$_3$	51.8(52.1)	4.7(5.0)	6.8(7.0)	546	4.9
Mn(phenglydisal-5-NO_2)(H_2O)$_3$	46.7(46.4)	3.2(3.5)	12.3(12.3)	515	4.7
Mn(phenglydisal-3-OMe,5-Br)(H_2O)$_{1.5}$	42.9(43.0)	3.1(3.2)	6.0(6.3)	642–643	5.0
Mn(phenglydisal-3-Br,5-Cl)(H_2O)	39.3(39.4)	1.9(2.1)	6.3(6.3)	650–656	4.8

[a] Found (calculated). [b] Peaks corresponding to $[MnL]^+$.

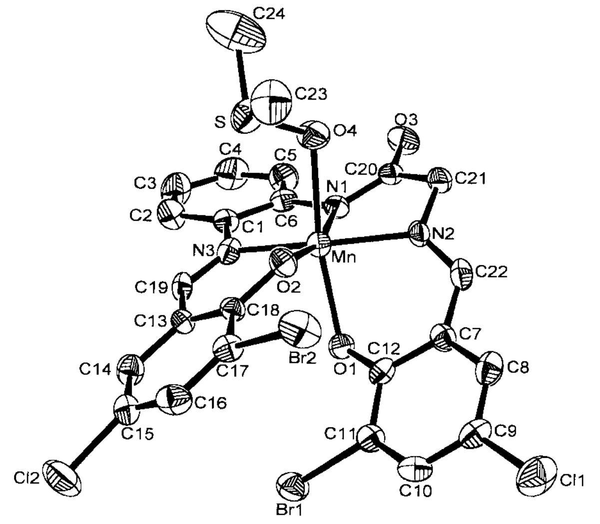


Fig. 1 An ORTEP view of the crystal structure of [Mn(phenglydisal-3-Br,5-Cl)(dmso)] **3**. Ellipsoids are drawn at 50% probability.

Table 5 Crystal data and details of refinement for the complex [Mn(phenglydisal-3-Br,5-Cl)(dmso)]

Formula	$C_{24}H_{18}Br_2Cl_2MnN_3O_4S$
M	730.13
Crystal size/mm	0.35 × 0.13 × 0.10
Crystal system	Monoclinic
Space group	$P2_1/n$
a/Å	8.472(2)
b/Å	21.591(4)
c/Å	14.512(3)
β/°	96.84
V/Å^3	2635.6(10)
T/K	293(2)
Z	4
D_c/g cm^{-3}	1.840
F(000)	1440
μ/mm^{-1}	3.852
Reflections collected	2519
No. unique reflections	2519
R	0.0462
R′	0.0462

Table 6 Selected bond lengths (Å) and angles (°) for [Mn(phenglydisal-3-Br,5-Cl)(dmso)] **3**

Mn–O(2)	1.915(5)	Mn–N(2)	2.015(6)
Mn–N(1)	1.953(6)	Mn–O(1)	2.111(5)
Mn–N(3)	1.989(6)	Mn–O(4)	2.287(5)
O(2)–Mn–N(1)	164.4(2)	N(3)–Mn–O(1)	97.0(2)
O(2)–Mn–N(3)	90.4(2)	N(2)–Mn–O(1)	83.8(2)
N(1)–Mn–N(3)	82.1(3)	O(2)–Mn–O(4)	81.6(2)
O(2)–Mn–N(2)	108.5(2)	N(1)–Mn–O(4)	86.1(2)
N(1)–Mn–N(2)	79.8(3)	N(3)–Mn–O(4)	98.7(2)
N(3)–Mn–N(2)	161.0(3)	N(2)–Mn–O(4)	85.9(2)
O(2)–Mn–O(1)	84.5(2)	O(1)–Mn–O(4)	159.0(2)
N(1)–Mn–O(1)	109.8(2)		

Synthesis and characterisation of manganese complexes

These manganese complexes were prepared following a variation of the Boucher method reported by us.[15]

The manganese compounds obtained *via* this synthetic route, in high yield, are light or dark brown powdery solids, which are air and heat stable. They are insoluble or sparingly soluble in water and common organic solvents but most are quite soluble in polar aprotic co-ordinating solvents such a dmf and dmso.

Elemental analyses (Table 4) indicate that the manganese complexes have the general stoichiometry Mn(phenglydisal-R)(H_2O)$_n$, suggesting that they are neutral. Molar conductivity measurements in 10^{-3} M dmf solutions, in the range 4–7 Ω^{-1} cm^2 mol^{-1}, show the non-electrolyte behaviour of these complexes,[16] in agreement with this.

Crystal structure of [Mn(phenglydisal-3-Br,5-Cl)(dmso)] 3

Diffusion of dichloromethane into a dmso solution of Mn(phenglydisal-3-Br,5-Cl)(H_2O) yielded dark brown crystals suitable for X-ray diffraction studies. The crystalline compound [Mn(phenglydisal-3-Br,5-Cl)(dmso)] **3**, consists of discrete neutral complex molecules with one co-ordinated molecule of dmso. An ORTEP view of [Mn(phenglydisal-3-Br,5-Cl)(dmso)] **3** is shown in Fig. 1. Experimental details are given in Table 5 and selected bond lengths and angles in Table 6.

The geometry around the Mn atom can be described as distorted octahedral, where the helical trianionic pentadentate ligand wraps around the Mn(III) centre *via* the amide nitrogen atom [N(1)], the two imine N-atoms [N(2), N(3)] and one phenol O-atom [O(2)] to fill the equatorial positions. The remaining phenol O-atom [O(1)] occupies an apical position because of the twisted arrangement of the asymmetric helical ligand. A capping dmso molecule completes the co-ordination polyhedron. Thus, the compound can be described as a mononuclear single-stranded helical Mn(III) complex, a type of compound that, to our knowledge, has not been previously described in the literature. There are some previous examples[17–19] of mononuclear helical complexes, including some of the first row, but this structure introduces some remarkable novelties:

1. Manganese(III) helical complexes have not been previously reported.

2. Whilst ligands used in literature in the isolation of helical complexes are generally symmetric, with a spacer group separating two identical arms, here, the ligand is asymmetric, with two clearly different arms.

3. This is the first helical manganese(III) complex with a Schiff base acting as a trianionic and pentadentate ligand.

The twisted disposition of the ligand seems to be favoured by the small size of the metal centre, which cannot accommodate a planar N_3O_2 compartment if it adopts a totally flat arrangement. Thus, a possible shortening of the bite angles and the subsequent steric hindrance, induced by the bromine substituents on the terminal aromatic rings, added to the strong

Table 7 ^{1}H NMR data and cyclic voltammetry for the complexes

	^{1}H NMR		Redox potentials[a]			
Complex	–CH_2–	H_{arom}	E_{ox}/V	E_{red}/V	$\Delta(E_{ox} - E_{red})$	$E_{1/2}$
Mn(phenglydisal)$(H_2O)_4$	28.45	−10.17, −12.07, −22.91, −38.37	−0.05	−0.44	0.39	−0.245
Mn(phenglydisal-5-Br)$(H_2O)_2$	27.87	−16.75, −23.03, −34.13	0.256	−0.373	0.63	−0.059
Mn(phenglydisal-3-OEt)$(H_2O)_3$	23.82	−9.53, −11.59, −22.1, −35.44	—	—		
Mn{phenglydisal-4,6-$(OMe)_2$}$(H_2O)_3$	29.53	−8.09, −8.99, −19.96, −25.5	−0.192	−0.444	0.252	−0.318
			0.612	0.520	0.092	0.566
Mn(phenglydisal-5-NO_2)$(H_2O)_3$	28.75	−16.66, −23.98, −33.74	0.404	−0.594	0.998	−0.095
Mn(phenglydisal-3-OMe,5-Br)$(H_2O)_{1.5}$	25.63	−9.85, −14.59, −24.71, −33.90	−0.021	0.111	0.09	−0.066
			0.805	—		
Mn(phenglydisal-3-Br,5-Cl)(H_2O)	23.19	−7.01, −25.54	0.010	−0.086	0.07	−0.048
			0.856	—		

[a] Potentials *vs*. SCE.

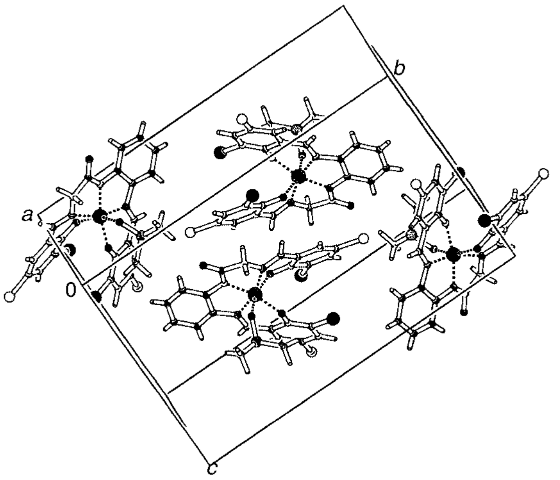


Fig. 2 The unit cell of [Mn(phenglydisal-3-Br,5-Cl)(dmso)] **3** showing the *P*- and *M*-handed isomers.

tendency of Mn(III) to adopt octahedral co-ordination geometries, probably induce the twisting. Finally, as the manganese atom requires an additional dmso molecule to fulfil its stereochemical requirements, we can also classify this compound as unsaturated.[17] Both right- (*P*) and left-handed (*M*) helixes[17] can be simultaneously observed, in 50% yield, in the unit cell, as shown in Fig. 2.

The Mn–N and Mn–O distances are typical of manganese(III) complexes[6] and corroborate complete deprotonation of the ligand. The Mn–O(4) distance of 2.287(5) Å, and the bond angles around the sulfur atom, are also typical of a dmso molecule co-ordinated to a metal centre.[20,21]

The deviation from an ideal octahedral geometry is shown by the wide range of angles observed around the metal centre [from 79.8(3) to 108.5(2)°], as well as by the interaxial angle O(4)–Mn–O(1) of only 159.0(2)°. The deviation of the equatorial plane from planarity further reinforces this distortion [maximum deviation from the least-squares calculated plane formed by O(2), N(3), N(1) and N(2) is *ca.* 0.165 Å, with the manganese atom *ca.* 0.082 Å below this plane]. This plane also shows a saddle shape distortion, with O(2) and N(1) displaced above and N(2) and N(3) below the mean calculated plane.

This ligand would be expected to show a high degree of planarity owing to the conjugation and presence of only one sp^3 atom in the chelate rings [C(21)]. However the C(12)–C(7)–C(22)–N(2) torsion angle of 26.2° is surprisingly high considering its conjugation. Consequently, the chelate ring formed by O(1)C(12)C(7)C(22)N(2) shows the most significant loss of planarity (*ca.* +0.153 Å), instead of the theoretically more flexible second chelate ring. Likewise, the angles between calculated chelate planes (20.7–22.8°) show a rather regular screwing for this thread. Despite the ligand twisting, the two terminal six-membered chelate rings form an angle of only 32.3°, with the two closest non-bonding atoms [C(11) and C(17)] separated by *ca.* 3.63 Å, which is an approximate measure of the helical pitch. Additionally, it can be clearly observed in the crystal structure, that the wrapping angle is slightly higher than 360°.

Mass spectrometery and IR spectroscopy

Fast atom bombardment (FAB) mass spectra show peaks (Table 4) relating to fragments of the form $[MnL]^+$, indicating ligand co-ordination to the metal centre.

This co-ordination is also supported by the IR spectra, which are very similar for all the complexes. Thus, a strong band at *ca.* 1600 cm^{-1}, attributable to ν(CN), show a shift to lower energy compared with the free-base values and indicates the co-ordination of the ligand to the metal through both imine nitrogen atoms. In addition, bands due to the amide I [ν(CO)] and the amide II [δ(NH) + ν(CN)] mode undergo negative shifts, compatible with the participation of the amide nitrogen atom in co-ordination to the metal.[22] Additionally, all complexes exhibit bands centred at *ca.* 3400 cm^{-1} in accord with the presence of co-ordinated and/or lattice water.

Finally, the absence of strong bands at *ca.* 1100 cm^{-1} indicates the absence of perchlorate anions in these manganese compounds.

^{1}H NMR studies

^{1}H NMR studies were undertaken using dmso-d_6 as solvent. The interpretation of the data was based on findings of Pecoraro and co-workers[23] and also on our own results[10,24] for Mn(III) complexes with related Schiff bases. These data are presented in Table 7.

The spectra contain between three and five proton resonances that lie outside the diamagnetic region (δ *ca.* 0–10). Two, three or four signals are observed between δ −7 and −39, which are assigned to the protons in positions 4 and 5 on the aromatic rings, in accordance with Pecoraro's observations[23] and with previous results reported by us.[10,24]

Additionally, a broad peak observed downfield ($\delta \approx 25$) can be assigned to the aliphatic protons of the methylene bridge.[10]

These data serve to substantiate the formation of manganese(III) complexes.

Magnetic and electrochemical behaviour of complexes

Values for the magnetic moments of the complexes at room temperature (Table 4) are very close to the spin only values of 4.9 μ_B, expected for a high spin magnetically dilute d^4 manganese(III) ion, indicating little or no antiferromagnetic interaction. This is in agreement with the ^{1}H NMR data and further confirms the trianionic behaviour of the ligands.

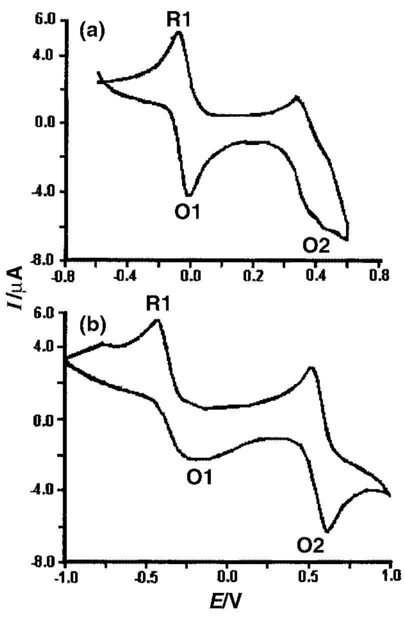


Fig. 3 Cyclic voltammograms for (a) Mn(phenglydisal-3-Br,5-Cl)(H_2O) and (b) Mn{phenglydisal-4,6-$(OMe)_2$}$(H_2O)_3$.

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 7 and typical voltammograms are shown in Fig. 3.

In general all voltammograms show a reductive process at negative potentials, which we assign to the reduction of manganese(III) to manganese(II).[6b,d,15] This process is irreversible for most of the complexes but some of them present an important degree of reversibility [Fig. 3(a)].

Three of these compounds show an oxidative process that can be assigned to the oxidation of manganese (III) to manganese(IV). It is interesting that Mn{phenglydisal-4,6-$(OMe)_2$}$(H_2O)_3$ [Fig. 3(b)] shows a quasireversible wave centred at 0.566 V. This potential is lower than those found in manganese(III) complexes with symmetrical[25] and asymmetrical Schiff bases.[10] Hence, it seems obvious that manganese(IV) is significantly stabilised by these ligands with hard donor atoms, especially when an electron-releasing substituent is introduced.[7,8,26] Unfortunately the low solubility of the complex Mn(phenglydisal-3-OEt)$(H_2O)_3$ in dmf prevented its study by voltammetry.

As a result of all these studies, and considering that Mn(III) is very prone to adopt octahedral environments when co-ordinated to Schiff bases, it seems probable that all these compounds present this type of geometry. The N_3O_2 donor ligand presumably occupies five co-ordination sites, whilst a water molecule would complete the co-ordination sphere in the solid state. This latter ligand appears to be extremely labile to solvent exchange, as revealed by X-ray crystallography for **3** when recrystallisation was from dmso. The weakness of the Mn–OH_2 bond is also shown by the FAB studies, where no peaks indicating co-ordinated water were observed in agreement with other previous results.[6]

Conclusion

Asymmetrical potentially trianionic and pentadentate Schiff base ligands, containing an amido group, readily stabilise neutral manganese(III) complexes. The X-ray crystal structure of [Mn(phenglydisal-3-Br,5-Cl)(dmso)] **3** shows that this type of ligand can twist and afford mononuclear single-stranded helical complexes, previously unreported for Mn(III) ions. Finally, the electrochemical study of the complexes suggests that manganese can adopt an oxidation state of +IV in the presence of this kind of ligand.

Experimental

Chemicals

Chemicals of the highest commercial grade available (Aldrich) were used as received.

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. IR spectra were recorded as KBr pellets on a Bio-Rad FTS 135 spectrophotometer in the range 4000–600 cm^{-1}. Mass spectrometry (electron 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. Room temperature magnetic susceptibilities were measured using a Digital Measurement system MSB-MKI, calibrated using mercury 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 a 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, and 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 the three-step method shown in Scheme 1.

Synthesis of *N*-(2-aminophenyl)-2-[(phenylmethoxy)carbonylamino]ethanamide 1. To a solution of carbobenzyloxyglycine (9.67 g, 46.20 mmol) in thf (100 cm^3) were added *o*-phenylenediamine (5.0 g, 46.20 mmol) and *N*,*N′*-dicyclohexylcarbodiimide (9.54 g, 46.20 mmol). This mixture was stirred at room temperature for 4 h.[13] The insoluble *N*,*N′*-dicyclohexylurea was removed by filtration and the solvent replaced by ethyl acetate (100 cm^3). Addition of light petroleum (bp = 40–60 °C) afforded 11.3 g (37.80 mmol) (82%) of amine **1** (Found: C, 64.0; H, 5.9; N, 13.7. Calc. for $C_{16}H_{17}N_3O_3$: C, 64.2; H, 5.7; N, 14.0%). ^1H NMR (dmso-d_6): δ 3.82 (d, 2H), 4.86 (s, 2H), 5.08 (s, 2H), 6.52 (t, 1H), 6.70 (d, 1H), 6.89 (t, 1H), 7.13 (d, 1H), 7.37 (m, 5H), 7.54 (t, 1H), 9.18 (s, 1H). ^{13}C NMR (dmso-d_6): δ 48.2 (CH_2), 69.6 (CH_2), 115.3–140.9 (C_{arom}), 157.8 (CO), 168.2 (CO). IR (KBr, cm^{-1}): ν(NH) 3473m, ν(NH_2), 3336s, 3383m and 3268m, ν(amide I) 1708vs, 1684vs and 1674vs, ν(amide II) 1623vs and 1544vs. Mp 145 °C. Mass spectrometry (EI): *m*/*z* 299.3.

Synthesis of 2-amino-*N*-(2-aminophenyl)ethanamide 2. A solution of **1** (10.00 g, 33.40 mmol) in ethanol (300 cm^3) was mixed with cyclohexene (5 cm^3, in excess of the molar proportion required) and 2.0 g of commercial 10% Pd–C catalyst (catalyst : substrate ratio 1 : 5 by weight). The mixture was refluxed for 15 min, filtered from the catalyst, the catalyst washed with ethanol, and the combined filtrates evaporated under reduced pressure[14] to give the deprotected amine **2** (yield 4.46 g, 81%) (Found: C, 57.9; H, 6.6; N, 25.5. Calc. for $C_8H_{11}N_3O$: C, 58.2; H, 6.7; N, 25.4%). ^1H NMR (dmso-d_6): δ 3.35 (s, 2H), 5.05 (s, 2H), 6.53 (t, 1H), 6.72 (d, 1H), 6.80 (d, 1H), 7.05 (t, 1H). ^{13}C NMR (dmso-d_6): δ 48.6 (CH_2), 115.4–146.8 (C_{arom}), 173.8 (CO). IR (KBr, cm^{-1}); ν(NH) 3416s, ν(NH$_2$) 3323s and 3200m, ν(amide I) 1680s, ν(amide II) 1635s. Mp 149 °C. Mass spectrometry (EI): *m/z* 165.1.

Preparation of Schiff base ligands. 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$_3$phenglydisal-3-Br,5-Cl. Amine **2** (0.76 g, 4.6 mmol) and 3-bromo-5-chlorosalicylaldehyde (2.18 g, 9.2 mmol) were dissolved in methanol (100 cm^3) and the solution was brought to reflux. The volume of the resulting solution was reduced over 3 h to *ca.* 50 cm^3, using a Dean–Stark trap and the solution 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 the prepared ligands was checked by elemental analysis, mass spectrometry (Table 1), IR (Table 2) and ^{1}H NMR spectroscopy (Table 3). The ^{13}C NMR spectra of all the ligands in dmso-d$_6$ show 17 signals corresponding the aromatic, imine and carbonyl carbon atoms, which lie in the range δ 108.1–168.2. Additionally, the methylene carbon of the chain and the methoxy and ethoxy substituents, when present, give separate signals below δ 70.

Synthesis of the complexes

The synthesis is typified by the preparation of [Mn(phenglydisal-3-Br,5-Cl)(H$_2$O)]: To a suspension of H$_3$-phenglydisal-3-Br,5-Cl (0.50 g, 0.83 mmol) in methanol–ethanol (1 : 1, 80 cm^3), manganese(II) perchlorate hexahydrate (0.33 g, 0.91 mmol) dissolved in methanol (10 cm^3) was added and the mixture stirred for 12 h. Then an aqueous solution of 10 M NaOH (1 cm^3) was added and a rapid change of the solution colour intensity was observed (**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 three days, the solid formed was collected by filtration, washed with water and diethyl ether and dried *in vacuo*. The complexes were obtained in high yield and with high purity.

Crystallographic measurements

Crystal data and refinement details are given in Table 5.

Crystals of **3** suitable for single X-ray diffraction studies were obtained as previously described. Data were collected at 293 K using a Nicolet P3 diffractometer employing graphite-monochromated Mo-Kα (λ = 0.71073 Å) radiation, using θ–2θ scans. The structure was solved by direct methods[27,28] and refined by full-matrix least squares on F^2. An analytical absorption correction was applied. All hydrogen atoms were included in calculated positions.

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