Synthesis and Characterisation of some New Manganese(II) and Manganese(III) Complexes of Tetradentate Schiff-base Ligands and their Reaction with Molecular Oxygen

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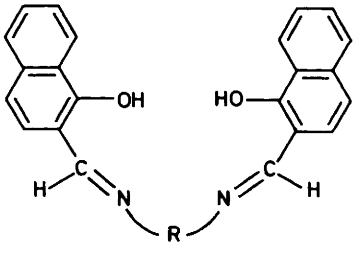
Some new manganese complexes containing tetradentate Schiff-base ligands (H_2L) derived from 1-hydroxy-2-naphthaldehyde and aliphatic diamines, $H_2N(CH_2)_nNH_2$ [n = 2, 3, 4, or 10; H_2L = *NN'*-ethylene-, propane-1,3-diyl-, butane-1,4-diyl-, and decane-1,10-diyl-bis(1-hydroxy-2-naphthylmethyleneimine)], have been synthesised. The structure and reactivity of the manganese(II) complexes critically depends on n. Thus, planar [MnL] are formed for n = 2, 4, or 10, but for n = 3 the pseudo-octahedral [$MnL(H_2O)_2$] is obtained. These manganese(II) species absorb approximately 0.5 mol O_2 per mol of Mn to form dimeric di-μ-oxo manganese(IV) complexes [{MnL(O)}$_2$], but this reaction in *NN*-dimethylformamide is surprisingly much faster for the complex [$MnL(H_2O)_2$] than for the planar species. In addition some manganese(III) complexes [$MnL(H_2O)$]ClO_4 have been obtained.

Complexes of manganese involving derivatives of salicylaldehyde and aliphatic amines have received considerable attention,[1-10] partly prompted by the role manganese ions, in close proximity, are thought to play at the dioxygen evolving site of photosystem II of green plant photosynthesis.[11-15] Thus, we have recently shown that visible irradiation of an aqueous solution of [{Mn(salpd)(H_2O)}$_2$][ClO_4]$_2$ [salpd = propane-1,3-diyl-bis(salicylideneiminate)] and quinone results in the evolution of dioxygen and the production of hydroquinone.[16,17]

We are extending our investigations to the more unusual N_2O_2 Schiff-base ligands (**I**) derived from 1-hydroxy-2-naphthaldehyde and aliphatic diamines; studies of similar ligands to these with copper(II)[18] and cobalt(II)[19] have been reported. We now wish to report our observations on the reaction of manganese(II) with these new ligands and the subsequent oxidation of the resulting complexes to yield higher-valent manganese species.


(**I**)

	R
H_2napen	$(CH_2)_2$
H_2nappn	$(CH_2)_3$
H_2napbu	$(CH_2)_4$
H_2napdec	$(CH_2)_{10}$

Experimental

The ligands H_2L, (**I**), were prepared by standard methods. Typically, a solution of the diamine (0.06 mol) in anhydrous ethanol (50 cm^3) was added to a rapidly stirred solution of 1-hydroxy-2-naphthaldehyde (0.1 mol) in ethanol (50 cm^3) in a 250-cm^3 round-bottomed flask. On completion of the addition the mixture was refluxed for 30 min. On cooling to room temperature a yellow solid crystallised, which was filtered off, washed with ethanol and dry diethyl ether (2 × 50 cm^3), and dried *in vacuo*. This method was applicable to all ligands and yields were almost quantitative based on the aldehyde. Elemental analyses, %Found (%Calc.): H_2napen: C, 78.2 (78.6); H, 5.2 (5.4); N, 7.5 (7.6); H_2nappn: C, 78.6 (78.9); H, 5.6 (5.7); N, 7.2 (7.3); H_2napbu: C, 78.9 (78.6); H, 6.1 (6.1); N, 7.1 (7.1); H_2napdec: C, 79.7 (80.0); H, 7.8 (7.5); N, 5.6 (5.8).

Preparations.—Complexes (**1**)—(**4**). The ligand (0.01 mol) suspended in dioxygen-free hot ethanol (150 cm^3) was mixed with solid NaOH (0.02 mol). When the base had dissolved a solution of manganese(II) acetate tetrahydrate in dioxygen-free ethanol (50 cm^3) was added dropwise to the ligand solution. The mixture was further refluxed with stirring for 1 h under argon. After cooling the resulting solid was filtered off, washed with dioxygen-free ethanol (3 × 20 cm^3), and dried *in vacuo*. The complexes were stored and handled under dry nitrogen; yields were almost quantitative.

Complexes (**5**)—(**8**). These manganese(III) Schiff-base complexes were prepared in an identical manner to that previously described,[17] giving yields of *ca.* 40%. The complexes are stable in air.

Complexes (**1**)—(**4**) have limited solubility in *NN*-dimethylformamide (dmf). Complexes (**5**)—(**8**) are somewhat soluble in dmf, and all complexes are insoluble in acetone, ethanol, and methanol.

Oxygenation Studies.—The reaction of the manganese(II) complexes with dioxygen was followed by monitoring changes in the u.v.-visible spectrum as a function of time. Quantitative absorption of dioxygen was also measured in an apparatus (essentially a gas burette, gas reservoir, and uptake flask immersed in a constant temperature bath) which is fully described elsewhere.[20] Dioxygen uptake by solvent blanks was also determined.

Physical Measurements.—These were carried out as previously described.[17]

Table 1. Analytical data and physical properties of complexes (**1**)—(**8**)

Complex	Colour	$\mu_{eff.}$	$g_{eff.}$	Analysis* (%) C	H	N	Cl	Mn
(**1**) [Mn(napen)]	Yellow	5.5	2.000	69.7 (68.7)	4.4 (4.3)	5.9 (6.7)		
(**2**) [Mn(nappn)(H_2O)$_2$]	Buff	5.8	2.000, 6.000	62.9 (63.9)	4.7 (4.7)	5.4 (5.9)		11.6 (11.7)
(**3**) [Mn(napbu)]	Yellow	5.6	2.000	69.0 (69.9)	5.3 (4.9)	6.1 (6.3)		
(**4**) [Mn(napdec)]	Yellow	5.8	2.000	70.1 (72.2)	6.1 (6.0)	4.9 (5.3)		
(**5**) [Mn(napen)(H_2O)]ClO_4	Reddish brown	4.9		52.2 (53.7)	3.3 (3.8)	5.4 (5.2)	7.1 (6.6)	10.3 (10.2)
(**6**) [Mn(nappn)(H_2O)]ClO_4·H_2O	Light brown	4.9		52.1 (52.8)	3.6 (4.3)	5.5 (4.9)	6.7 (6.2)	9.5 (6.7)
(**7**) [Mn(napbu)(H_2O)]ClO_4	Green	4.4		54.5 (55.3)	4.4 (4.3)	5.1 (4.9)	6.1 (6.3)	
(**8**) [Mn(napdec)(H_2O)]ClO_4	Green	4.6		60.9 (59.0)	5.5 (5.5)	4.7 (4.3)	4.7 (5.5)	

* Calculated values are given in parentheses.

Table 2. Significant i.r. bands (cm^{-1}) for complexes[a] (**1**)—(**8**)

Complex	ν(C=N)[b]	ν(ClO_4^-)	ν(Mn–O)	ν(Mn–N)
(**1**)	1 615 (1 625)		424	370
(**2**)	1 610 (1 625)		425	345
(**3**)	1 610 (1 630)		420	365
(**4**)	1 620 (1 640)		420	345
(**5**)	1 600 (1 625)	1 100	420	380
(**6**)	1 600 (1 625)	1 100	422	380
(**7**)	1 615 (1 630)	1 100	420	380
(**8**)	1 620 (1 640)	1 090	424	380

[a] As Nujol mulls. [b] Values for the free ligands are given in parentheses.

Results and Discussion

Two types of complex were isolated in the first part of this study, the manganese(II) complexes [MnL] (L = napen, napbu, or napdec) or [Mn(nappn)(H_2O)$_2$] and the manganese(III) complexes [MnL(H_2O)]ClO_4,[21] Table 1. These complexes, (**1**)—(**8**), all exhibit very similar i.r. features assignable to Schiff-base ligands.[6,7,16–19] All show a shift to lower energy of the ν(C=N) in the free ligand, indicating complexation of the ligand in the dianionic tetradentate mode,[22] Table 2. In addition, some complexes exhibit a broad absorption centred at *ca.* 3 400 cm^{-1}, assigned to ν(OH) of water. Other significant absorptions are listed in Table 2.

The electronic spectra of complexes (**1**)—(**4**) were obtained in dmf in an inert atmosphere, and are characterised by well defined bands at 404 and 424 nm and a well defined shoulder at 375 nm. The spectra of the manganese(III) complexes (**5**)—(**8**) have the general shape and intensity expected for manganese(III) d^4 Schiff-base complexes in a pseudo-octahedral environment,[7] Figure 1.

The room-temperature magnetic moments of complexes (**1**)—(**4**) are consistent with the high-spin d^5 configuration, as are those for complexes (**5**)—(**8**) for the high-spin d^4 configuration, Table 1. Complexes (**1**)—(**4**) exhibit strong broad e.s.r. signals centred at $g = 2$, consistent with manganese(II).[23] In addition, complex (**2**) exhibits a broad weak signal at $g = 6$, Table 1. The manganese(III) complexes do not exhibit any e.s.r. spectra at room temperature.

All of the above data are consistent with a planar stereochemistry for complexes (**1**), (**3**), and (**4**), pseudo-octahedral for complex (**2**), while complexes (**5**)—(**8**) are probably aqua-bridged dimers, (**II**), as evidenced[17] by their reduced magnetic moments and fast atom bombardment mass spectra. In addition to the basic stereochemistry around the manganese, complexes (**3**), (**4**), (**7**), and (**8**) may be oligomeric or polymeric as a result of their long methylene chains.

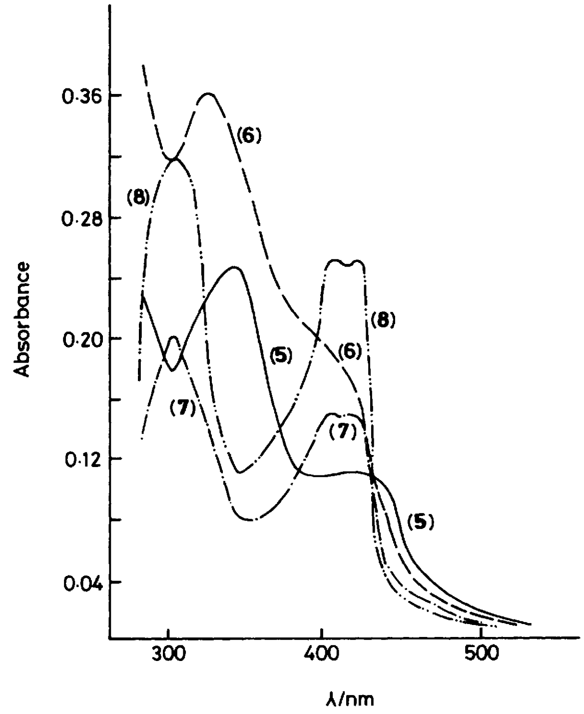
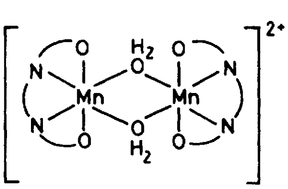


Figure 1. Electronic spectra of the manganese(III) complexes (**5**)—(**8**) in dmf



(**II**)

It is noteworthy that of the four manganese(II) complexes isolated, from identical preparative conditions, three are planar [MnL] species whereas the ligand with the trimethylene backbone yields the pseudo-octahedral complex [Mn(nappn)(H_2O)$_2$]. We have noted before that the stereochemistry[16,17,19,22,24] and subsequent reactivity[16,17,19] of metal complexes of tetradentate N_2O_2 donor Schiff-base ligands is critically dependent on the nature of the ligand central backbone.

Table 3. Analytical data and physical properties of complexes (**9**)—(**11**)

Complex	Colour	$\mu_{eff.}$	Analysis[a] (%) C	H	N	Mn	n_{O_2}/n_{M_n}[b]
(**9**) $[\{Mn(napen)(O)\}_2]$	Brown	1.9	65.3 (65.9)	5.3 (4.1)	6.0 (6.4)	10.3 (12.6)	0.47
(**10**) $[\{Mn(nappn)(O)\}_2]\cdot 2H_2O$	Dark brown	1.7	62.5 (63.3)	4.9 (4.3)	6.7 (6.2)	11.9 (12.0)	0.53
(**11**) $[\{Mn(napbu)(O)\}_2]\cdot 4H_2O$	Brown	2.4	61.1 (62.3)	5.5 (4.8)	6.8 (5.6)	12.3 (11.0)	0.54

[a] Calculated values are given in parentheses. [b] Four uptakes were done per complex; agreement was ±3.6% maximum.

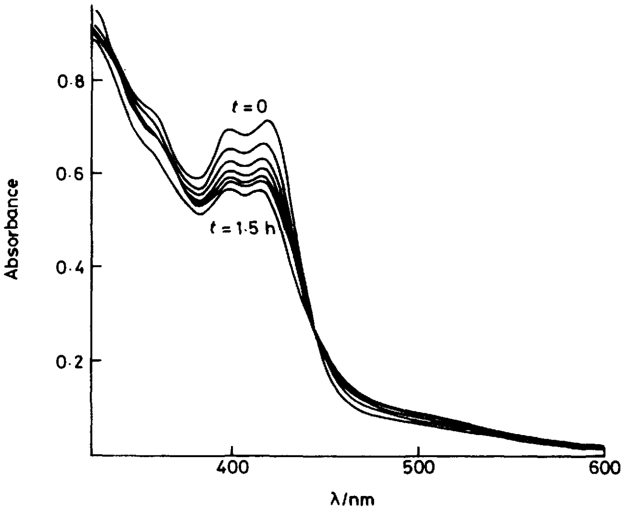


Figure 2. Repetitive scan for the oxygenation of [Mn(napen)] (**1**) in dmf at room temperature

However, we also observe here an even more subtle ligand structure effect. We have already reported[18] the isolation of $[MnL'(H_2O)_2]$ (L′ is a very similar ligand to napen, being derived from the 2-hydroxy-3-naphthaldehyde precursor) and the fact that we only isolated [Mn(napen)] in this study is a further indication of the critical effects ligand structure can have on complex stoicheiometry. Further effects of this can be seen in the i.r. spectra; for example, ν(Mn–O) is observed at 485 cm^{-1} for $[MnL'(H_2O)_2]$[18] but at 424 cm^{-1} for [Mn(napen)].

Reaction of the Manganese(II) *Complexes with Dioxygen*.—The passage of dioxygen through the yellow complexes (**1**)—(**3**) as slurries in dmf at 22 °C causes a colour change to brown. Bubbling argon through the brown slurry does not regenerate the original yellow colour of the complexes, strongly suggesting that the reaction is irreversible. We have measured the amount of O_2 absorbed by complexes (**1**)—(**3**) in dmf at room temperature, and this corresponds to 0.5 (±0.04) mol O_2 per mol of Mn, Table 3. Similar results have been observed for manganese(II) complexes containing tridentate ligands.[25]

We have observed some gross differences in the reaction of complexes (**1**)—(**3**) with dioxygen. Under the conditions employed, reaction of complex (**2**) with O_2 was complete in *ca.* 30 min, whilst for complexes (**1**) and (**3**) only slow oxidation occurred, taking *ca.* 20 h. It is unlikely that this represents merely solubility differences between (**2**) and (**1**) and (**3**). It is, perhaps, unwise to speculate on the underlying reasons for the observed gross differences in reaction rates, since these may be due to both differences in the overall structures of the individual complexes in solution or may be due to the preferred configuration of the individual ligands about the manganese.

The reaction of complexes (**1**)—(**3**) with O_2 was also followed by observing changes in the visible spectra during oxidation.

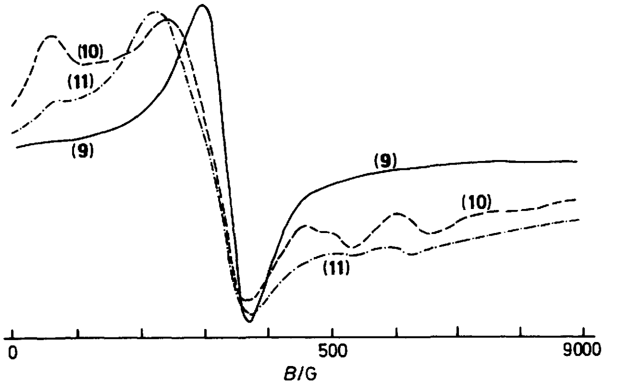
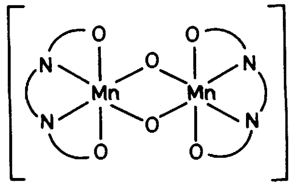


Figure 3. Solid-state e.s.r. spectra of the oxygenated manganese Schiff-base complexes (**9**)—(**11**) at room temperature



(III)

Figure 2 is a typical repetitive scan of an oxygenation reaction. The spectrum of complex (**1**) in dmf is characterised by the well defined bands at 404 and 424 nm which are ligand related (charge transfer). When dioxygen is admitted to the solution these bands diminish and shoulders appear at higher energy. In addition, a very weak band appears at *ca.* 500 nm assignable to a *d–d* transition on manganese(IV).[26]

The brown products formed during these quantitative absorptions of dioxygen were filtered off, washed with dry ethanol and further dried *in vacuo*. The analytical data for the new complexes (**9**)—(**11**) are listed in Table 3. The i.r. spectra of these compounds exhibit ligand bands essentially unchanged from those of their manganese(II) precursors, and, in addition there are some new medium intensity bands at 630, 600, and 580 cm^{-1} which are predicted to be characteristic of di-μ-oxo bridged manganese systems.[27] Room-temperature magnetic moments are listed in Table 3, but they do not distinguish between antiferromagnetically coupled high-spin manganese(III), d^4, or manganese(IV), d^3. However, all of the new complexes (**9**)—(**11**) are e.s.r. active, effectively ruling out manganese(III) species.[27–29] Figure 3 shows the solid-state e.s.r. spectra of complexes (**9**)—(**11**) at room temperature. The spectra are characterised by a strong broad signal at $g = 2$ and, in addition, complex (**10**) exhibits weaker signals at $g = 6$ and at higher field. The structure which fits all of the above evidence is (**III**).

As pointed out above, some manganese(II) complexes of tridentate Schiff-base ligands also take up dioxygen in a 1:0.5 Mn:O_2 ratio.[25] It is interesting to note, however, that the products were assigned as Mn^{III}–O_2–Mn^{III}, *i.e.* μ-peroxo dimers.

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