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New Manganese(II) and Copper(II) Complexes of Tetradentate N_2O_2 Schiff Base Ligands

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The study of transition metal complexes of Schiff base ligands has been extensive, as these ligands are available in a number of possible denticities and containing different donor atoms in addition to the imine groups.

We have had a particular interest in the Schiff base complexes of manganese; a review of this area has recently appeared [1]. Our interest in manganese complexes of oxygen/nitrogen donor systems stems from the fact that it is believed that high-valent manganese plays an essential and specific role in the dioxygen evolution mechanism of photosystem II, PPS II, in green plant photosynthesis [2–4]. Thus, we have recently shown that the visible irradiation of an aqueous solution of $[Mn(Saltm)(H_2O)]_2(ClO_4)_2$ [saltm = N,N′-propylenebis(salicylideneaminato)] and quinone results in the evolution of dioxygen and the production of hydroquinone [5]. Moreover, the fact that we have been able to isolate the novel manganese(II) carbonyl complex $[Mn(Salten)(CO)]_2(ClO_4)_2$ [salen = N,N′-ethylenebis(salicylideneaminato)] [6] indicates that complexes of manganese(III) with this type of O_2N_2 ligand system offers great potential for small molecule coordination and activation.

We are extending our investigations to more unusual O_2N_2 Schiff base ligands. NaphthalbenH$_2$ is essentially structurally similar to salenH$_2$, but it might be expected to absorb visible radiation more effectively than salenH$_2$; both salenben and anphthalben are structurally novel. Here we report our initial observations on their reaction with manganese(II) and copper(II) salts.

Results and Discussion

The new complexes are listed in Table I together with microanalytical and spectroscopic data. It is

TABLE I.

Compound	Colour	Analyses[a]				Infrared (cm^{-1})			Visible Reflectance (nm)	μ_{eff} (μ_B)	g_{eff}
		%C	%H	%N	%M	$\nu(C=N)$[b]	$\nu(M-O)$	$\nu(M-N)$			
Mn(naphthalen)$(H_2O)_2$	Yellow	62.7(63.0)	4.6(4.8)	6.0(6.1)	11.8(12.1)	1625	485	380	405, 395, 345	5.8	2.006
Mn(salben)$(H_2O)_2$	Yellow-Green	64.6(64.8)	4.5(4.6)	5.6(5.8)	11.3(11.5)	1610	460	375	405, 395, 340	5.8	2.032
Mn(naphthalben)$(H_2O)_2$	Red-Brown	69.8(70.2)	4.5(4.5)	4.8(4.8)	9.2 (9.5)	1620	485	380	405, 395, 340	5.8	2.054
Cu(naphthalen)(H_2O)	Green	64.2(64.4)	4.6(4.5)	6.2(6.3)	14.0(14.2)	1625	475	380	760	1.6	2.070
Cu(salben)(H_2O)	Green	65.8(66.2)	4.1(4.2)	5.7(5.9)	13.2(13.5)	1610	470	375	755	1.6	2.073
Cu(naphthalben)(H_2O)	Brown	71.1(71.4)	4.0(4.2)	4.7(4.9)	11.0(11.1)	1625	465	385	755	1.4	2.078

[a] Found (calculated). [b] $\nu(C=N)$ appears at 1635 cm^{-1} in all the free ligands.

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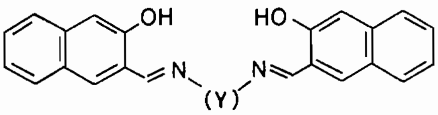
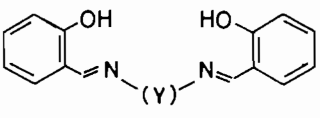


$Y = -C_2H_4-$, LH_2 = naphthalen

Y = $\underline{o}$-C_6H_4-C_6H_4-$\underline{o}$, LH_2 = naphthalben



Y = $\underline{o}$-C_6H_4-C_6H_4-$\underline{o}$, LH_2 = salben

somewhat surprising to note that, despite the structural differences in the ligands (ligands with the dimethylene backbone would be expected to chelate, whereas those with the rigid *o*-C_6H_4-C_6H_4-*o* backbone can probably only bridge), all three ligands form complexes with manganese(II), Mn(ligand)$(H_2O)_2$, and copper(II), Cu(ligand)(H_2O), of identical stoicheiometry.

All of the complexes exhibit ν(OH) of the, presumably, co-ordinated water molecules *ca.* 2750–2710 cm^{-1}, the energies of these absorptions suggesting H-bonding. The ν(C=N) absorption occurs in the range 1625–1610 cm^{-1}, there being a shift to lower energy from that of the free ligand. As well as indicating that the imine groups of the ligands are co-ordinated, a shift to lower energy may be taken as evidence of a dianionic tetradentate Schiff base co-ordination [7, 8]. In addition, bands occur in the ranges 485–460 cm^{-1} and 385–375 cm^{-1}, which may be assigned to ν(Mn–O) and ν(Mn–N), respectively [9], and which are absent in the spectra of the free ligands.

The electronic reflectance spectra of the manganese(II) complexes exhibit band maxima at similar energies but of different relative intensities. The room temperature magnetic moments, μ_{eff} = 5.8 μ_B, are indicative of five unpaired electrons per manganese and there is no evidence of spin pairing. The solid state X-band EPR spectra at room temperature exhibit an isotropic signal consisting of a pattern of six doublets.

We suggest the *cis* monomeric structure (**I**), for Mn(naphthalen)$(H_2O)_2$, and a polymeric structure, (**II**), for the other complexes. Molecular models indicate that a *cis* structure, (**I**), accommodates the tetradentate ligand with much greater ease than does a *trans* structure. Finally, we wish to point out that, whilst the complexes were sensitive to dioxygen when in contact with liquids, when dry they showed no sensitivity to dioxygen. This is quite remarkable as, for example, [Mn(salen)$(H_2O)_2$] readily oxidises in air.

The cupric complexes have reduced magnetic moments, μ_{eff} = 1.4–1.6 μ_B, indicating some spin-pairing. This could arise from dimer formation via bridging aqua ligands to give a six-co-ordinate species, or through a staching association via bridging oxygen atoms of the Schiff's base ligands.

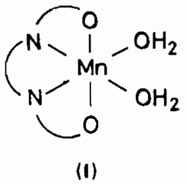
Experimental

Complex Preparation

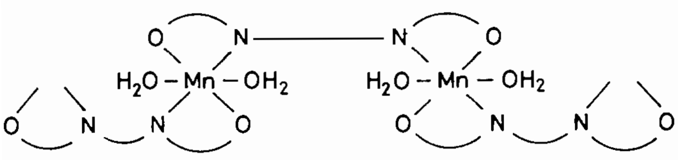
The complexes were prepared using a modification of the method of Miller and Oliver [10]. For example, the sodium salt of the ligand was prepared by mixing an aqueous solution of NaOH with an ethanolic solution of LH_2 in ethanol. The flask was flushed with N_2 and a solution of metal(II) acetate in a 50:50 H_2O/EtOH mixture (ligand: manganese ratio 1:1) was added with stirring. The complex precipitated almost immediately. The mixture was refluxed for 1 h, allowed to cool, and filtered under N_2 in a Schlenk apparatus. The complex was then washed with cold ethanol and dried *in vacuo*.

Physical Measurements

These were obtained as previously described [7]. All complexes are non-conductors in N,N'-dimethylformamide.



(I)



(II)

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