

Spectroscopic analyses of phenoxyl manganese (III) complexes

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Introduction

Many reactions use metalloproteins as catalysts. Galactose oxidase is a copper metalloprotein that represents an interesting example of cooperation between a metal and a radical to catalyse oxidation reactions. To model the Galactose oxidase active site, several biomimetic approaches have been developed. Consequently, a large number of phenoxyl copper (II) complexes have been synthesized. Although they provide good structural models, they exhibit a rather modest catalytic activity. The non-radical Manganese (III) complexes display more interesting activity. The goal of this work was to synthesize and characterize phenoxyl manganese (III) complexes. Possible analytical techniques available include: electrochemistry, UV/Vis and EPR spectroscopy. This article dealt with the UV/Vis spectroscopic analysis of these complexes.

Experimental section

Preparation of complexes

Complexes 1, 2 and 3 were prepared by dissolution of the ligand, with 1 molar equivalent of $Mn(OAc)_2 \cdot 4H_2O$, in a CH_2Cl_2 / EtOH mixture. Then the 3 complexes were precipitated by the addition of H_2O saturated with NaCl. The precipitates were filtered and dried with ether. Complexes 1 and 2 were purified by column chromatography over a silica gel with CH_2Cl_2 / MeOH (50:5)

UV/Vis spectroscopy

UV/Vis spectra are recorded at 298K with a Cary 50 spectrophotometer equipped with a temperature control, set at 298K. The path length of the quartz cell was 1,000cm. Low temperature UV/Vis spectra (248K) were recorded with a Cary 50 spectrophotometer equipped with Hellma low temperature immersion probe (1,000 cm path length quartz cell). The spectra were recorded with a complex solution of $5 \cdot 10^{-5}$ M in CH_2Cl_2 , before and after an addition of 1 equivalent part of tris(4-bromophenyl)aminiumhexachloroantimonate 10⁻²M in acetonitrile solution.

Results

The UV/vis spectra of 1, 2, and 3, in CH_2Cl_2 , were dominated by intense absorptions at 489, 329 and 356 nm respectively, and a low intensity shoulder, around 600 nm. The first bands corresponded to a charge transfer (CT) transition (n-d) combined with intraligand n-n* transition. The longer-wavelength band corresponded to d-d transitions.

After 1 equivalent part of oxidizer was added to 1 and 2, dramatic changes were observed in the spectra. This means that the oxidized species were less reactive at 25 °C. The spectrum of complex 3 did not change, following the addition of the oxidant. It is probable that tris(4-bromophenyl)aminiumhexachloroantimonate is not strong enough to oxidize this complex. Indeed, the presence of a NO_2 substitute, a strong electroattractant, does not enhance the oxidation process.

Upon addition of oxidizer, to the complexes 1 and 2, at 248K, a new band appeared at 786 and 714nm, respectively. These

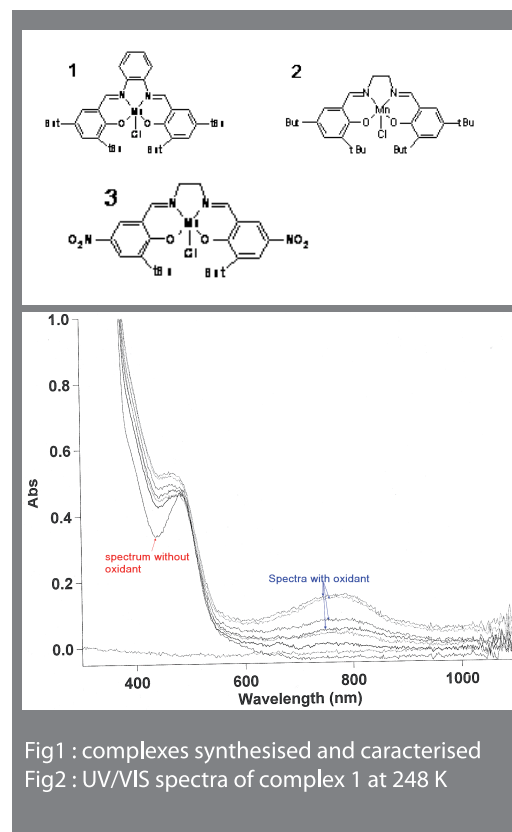


Fig1 : complexes synthesised and caracerised
Fig2 : UV/VIS spectra of complex 1 at 248 K

bands were not present prior to the addition of the oxidizer. According to a recent publication [1], this band is typical for Mn(IV) complexes, thus oxidation of 1 and 2 was metal-based rather than ligand-based. No radical Mn(III) complex could be detected. This preliminary study suggests that the nature of the ligand influences the oxidation potential and also the oxidation site localization.

[1] T.Kurahashi, A.Kikuchi, T.Tosha, Y.Shiro, T.Kitagawa,H.Fujii, Inorg. chem .2008, 47, 1674



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