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**PREFACE**

Mixed valent manganese complexes play an important role in the evolution of oxygen by water oxidation in Photosystem (PS II) of photosynthesis. Details regarding the structure of manganese site and the reaction mechanism are still ambiguous. However, some binuclear and tetranuclear complexes with polypyridyl, Schiff-base and related ligands in which the manganese is in (III, IV) oxidation states are proposed as good models. We desired to take advantage of the substitutional lability of Mn(III)(d⁴) site to prepare and characterise unsymmetrically ligated complexes. This has resulted in the isolation of complexes of the type \((\text{Mn}_{2}O_{2}L_{3}A)_{2}^{3+}\) where \(A=\text{dmf, py}\) and \((\text{Mn}_{2}O_{2}L_{3}A)_{2}^{3+}\) where \(A=\text{bpy, L=phen and A=phen, L=bpy}\). They have been characterised by i.r, electronic and e.s.r spectra. The studies on oxygen evolution in presence of Ce⁴⁺ suggest that the unsymmetrical complexes are better catalysts for water oxidation.

We had also planned to synthesise new Mn(III, IV) complexes with ligands related to bpy viz., dmbp, dmp, mmnp, tmnp, daf and daf-one with a view to modify the electron transfer rate. However, all our attempts in this direction using Mn²⁺ and oxidizing agents like MnO₄⁻, S₂O₈²⁻ as well as substitution on Mn(urea)₆³⁺ followed by disproportionation and dimerisation, were unsuccessful.

Since we have prepared several sterically hindered ligands for the above purpose, we surveyed the chemistry of other complexes of these ligands. The interesting aspects of the copper chemistry of these ligands especially their marked influence in the Cu⁺/Cu²⁺ potential prompted
us to prepare and study analogous silver complexes. We have obtained magnetically dilute double salts, \([\text{AgLNO}_3\text{]}\text{PF}_6\cdot\text{NH}_4\text{PF}_6\), with dmp and dmpb ligands while other ligands formed magnetically concentrated complexes. Detailed e.s.r studies were carried out on the double salts. These complexes were unstable and slowly disintegrated to give radicals which gave uninterpretable e.s.r spectra suggesting a novel electron transfer from \(\text{PF}_6^–\) to \(\text{Ag}^{2+}\) ion.

Our studies on the two different metals are separated into Section I and Section II for a convenient presentation.

In Section I the chemistry of dioxo-bridged manganese (III, IV) complexes are reported, beginning with a chapter giving details on mixed valent complexes in general, their historical importance, theory, classification and the literature on Mn(III, IV) complexes. The next chapter deals with the experimental section in which preparative methods are described along with the techniques used for the physical measurements and the computer simulation program used. The last chapter in this section gives a detailed discussion on the results of various analytical and spectral studies, as well as catalytic water oxidation in the presence of \((\text{NH}_4)_2\text{Ce(NO}_3\text{)}_6\).

In Section II, complexes of bivalent silver with sterically hindered ligands are reported. The first chapter gives a brief introduction to Ag(II) chemistry including a survey on bivalent silver complexes of heteroaromatic ligands. This is followed by a discussion on the analogous copper complexes with the above mentioned sterically hindered ligands. The second chapter describes the experimental proce-
dure adopted and the program for the computer simulation of e.s.r spectra. The last chapter gives the discussion of various analytical and spectral results obtained including a detailed interpretation of the e.s.r results on Ag(II) complexes of heteroaromatic ligands. These double salts lead to the formation of radicals which resulted in an uninterpretable e.s.r spectra. A survey of literature ruled out the possibility of silver cluster formation. Electron transfer from PF$_6^-$ to Ag$^{2+}$ is proposed and various radicals involving P and F, including the hitherto unknown PF$_6^-$ radical are considered as possible sources for the complex spectrum.

Some of the results presented in this thesis have been published or communicated in preliminary form.

