SUMMARY AND CONCLUSIONS

1. Ce(IV) is a good oxidising agent for synthesis of high-valent manganese complexes.

2. Formation of different cores \( \text{Mn}_2\text{O}_2\text{(OAc)} \), \( \text{Mn}_2\text{O}(\text{OAc})_2 \) and \( \text{Mn}_3\text{O}_4 \) and nuclearity (mono, di and tri) shows that the aqueous chemistry of manganese is quite complex and variation of ligand (bpy or phen), acid (\( \text{HClO}_4 \), \( \text{HNO}_3 \), \( \text{HOAc} \) and \( \text{H}_3\text{PO}_4 \)) and anion (\( \text{ClO}_4^- \), \( \text{PF}_6^- \), \( \text{Cl}^- \) and \( \text{Br}^- \)) resulted in the formation of different complexes.

3. Reactions in aqueous media are successful in preparing aquo-bound complexes. However, water coordination on the two metal centers in di- and tri- nuclear complexes are found to be in trans position. Formation of only one type of isomer (trans) is probably because of thermodynamic and kinetic factors responsible for preferential formation of one isomer over the other possible isomers.

4. In perchloric acid media, presence of acetate resulted in the formation of \([\text{Mn}_2\text{O}_2\text{(OAc)}\text{(H}_2\text{O})_2\text{(bpy)}_2\text{(ClO}_4^-)_3\text{H}_2\text{O}]\) compound while in the absence of acetate \([\text{Mn}_3\text{O}_4\text{(H}_2\text{O})_2\text{(bpy)}_4\text{(ClO}_4^-)_4\text{H}_2\text{O}]\) was obtained. This is true with bpy ligand; attempts with phen ligand were not successful because of precipitation of phen\(\text{HClO}_4\). On the other hand, in \(\text{HNO}_3\) medium, even in the presence of acetate, only \([\text{Mn}_3\text{O}_4\text{(H}_2\text{O})_2\text{(phen)}_2\text{(NO}_3^-)_4\text{H}_2\text{O}]\) is formed. Reactions with bpy in \(\text{HNO}_3\) are failed to
crystallise out probably because of high solubilities of the species present in solution. These results show, the reactivities of bpy and phen are different and variation of acid and bridging units will lead to the formation of different complexes.

5. Variable temperature magnetic susceptibility study on

\[ [\text{Mn}_2O_2(OAc)(H_2O)_2(bpy)_2](ClO_4)_3 \cdot H_2O \] shows relatively weak antiferromagnetic interactions \( J = -44.6 \text{ cm}^{-1} \); \( \chi = -2JS_1S_2 \) compared with the other known Mn(IV,IV) dimers.

6. Oxidation of manganese in acetic acid medium resulted in the formation of two compounds, \([\text{Mn}_2O(OAc)(H_2O)(NO_3)(bpy)_2]ClO_4 \cdot CH_3COOH\) and \([\text{Mn}_2O(OAc)(H_2O)_2(bpy)_2](ClO_4)_2\) from the same reaction mixture. Formation of the first compound as the major product shows the substitutional lability of the Mn(III) sites. Change of anion from ClO\(_4^-\) to PF\(_6^-\) results in the exclusive formation of first compound as PF\(_6^-\) salt. Unsymmetrical environment in the first compound effects the Mn-OH\(_2\) distance and shows a smaller Mn-OH\(_2\) distance (2.224 Å) compared with the value (2.315 Å) in the symmetrical environment of the second compound. Jahn-Teller distortions observed in both the complexes along trans-O\(_A\) -Mn-OAc bonds (O\(_A\) is the NO\(_3^-\) oxygen or water oxygen for the first compound and it is only water oxygen for the second compound).

7. Presence of Cl\(^-\) resulted in the formation of Mn(III) monomers

\([\text{Mn(phen)}_2Cl_2](NO_3)_2 \cdot 2.5CH_3COOH\) and \([\text{Mn(phen)}(H_2O)Cl_3]\). Both
the compounds show a Jahn-Teller distortion by axial elongation. The second compound shows the longest Mn-OH₂ bond (2.306 Å) of all the known Mn(III)-aquo bound monomers.

8. Mn(OAc)₃ in aqueous solutions leads to the formation of Mn(III,IV) complex, \([\text{Mn}_2 \text{O}_2 (\text{OAc})_2 (\text{H}_2 \text{O})_2 (\text{bpy})_2 ](\text{ClO}_4)_2 . \text{HNO}_3.\)

Observed structural deviation may be because of symmetry related disorder or particular type of Jahn-Teller distortion at the Mn(III) site.

9. Comparison of exchange parameter \(J\) with Mn-Mn distances shows a poor correlation for (III,IV) and (IV,IV) complexes. Detailed EHMO calculations will provide a better understanding of exchange interactions.

10. In general low yields of the present complexes shows that, characterisation of unisolated species in solution will provide further understanding of high-valent manganese chemistry in aqueous solution.

11. Formation of \([\text{Mn}_2 \text{O}_2 (\text{HPO}_4)_2 (\text{H}_2 \text{PO}_4)_2 (\text{bpy})_2 ] . \text{H}_2 \text{O}\) and \([\text{Mn}_2 \text{O}_2 (\text{H}_2 \text{O})_2 (\text{Br})_2 (\text{bpy})_2 ] \text{Br}\) are interesting and further structural studies on these complexes will help in understanding the reactions of aqueous solutions.

12. Though trans coordinated water complexes of manganese are not favorable for peroxy bridge formation (which is a key step in water oxidation reaction at WOC), the present complexes are interesting because of (i) uncommonly observed water coordination to high valent manganese (ii) possibility of
making magneto-structural correlations for dinuclear manganese complexes and (iii) possibility of using these complexes for chemical and photochemical oxidation of water, which aspect needs to be investigated in detail.