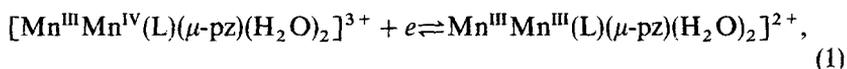


Studies on high-valent (≥ 2) dinuclear manganese complexes using a septadentate Schiff-base ligand in relation to manganese catalase enzymes

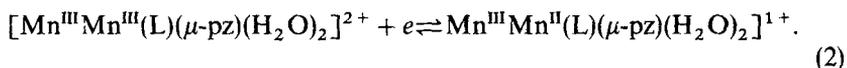
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A series of binuclear manganese(III)-manganese(III) complexes could be readily obtained, possessing the general formula $[\text{Mn}_2(\text{L})(\text{X})(\text{H}_2\text{O})_2]\text{Y}_2$ ($\text{X} = \text{Cl}^-$, OH^- , pz^- ; $\text{Y} = \text{Cl}^-$, $\text{pz}^- = 3,5$ -dimethylpyrazolate). These are synthesised and characterised using a septadentate ligand (H_3L) formed from the Schiff base condensation of triethylenetetramine and salicylaldehyde. Apart from the exogenous bridging ligand X , the ligand design provides a second bridging aryloxy oxygen as also a third bridging by the inbuilt imidazole ring in the ligand backbone. The Mn–Mn magnetic interaction is dependent on the presence and nature of X in the dinuclear complexes. Methanol solutions of the $[\text{Mn}_2^{\text{III}}(\text{PhO})]^{5+}$ complexes show the typical Mn^{III} $d-d$ electronic absorption bands in pseudotetragonal environment at around 650 nm and 500 nm respectively. $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ was used in appropriate stoichiometries to generate $\text{Mn}^{\text{III}}\text{Mn}^{\text{IV}}$ and Mn_2^{IV} complexes from $[\text{Mn}_2^{\text{III}}(\text{L})(\mu\text{-Cl})(\text{H}_2)_2]\text{Cl}_2$ in MeOH. The $[\text{Mn}_2(\text{L})(\mu\text{-pz})(\text{H}_2\text{O})_2]\text{Cl}_2$ complex shows a well-defined quasi-reversible cyclic-voltammetric response in MeOH for the $\text{Mn}^{\text{III}}\text{Mn}^{\text{IV}} - \text{Mn}^{\text{III}}\text{Mn}^{\text{III}}$ one-electron oxidative couple



and another response on the negative side of potential for the one-electron reductive couple



The X-band EPR spectra of the frozen (77 K) solution of the coulometrically-oxidised $\text{Mn}^{\text{III}}\text{Mn}^{\text{IV}}$ species in MeOH:toluene (1:1) glass exhibits only a six-line manganese hyperfine structure instead of the characteristic sixteen-line split pattern (e.g. S_2 state of Photosystem II). This may be due to its instability on the coulometric time scale resulting in transformation to a $[\text{Mn}^{\text{IV}}\text{L}]^+$ mononuclear species. The obtained results have relevance to the catalases which appear to possess a dinuclear Mn_2^{III} site with nitrogen based peripheral ligands. These complexes could also be considered as substrate-analogue-bound forms viz., aquo-catalase (resting form of the enzyme).

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