X- and Q-band EPR studies of a serious of homologues dinuclear Mn-complexes in varying valence states

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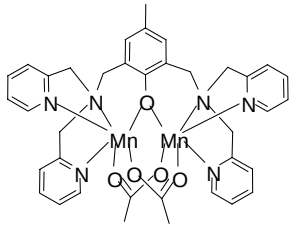
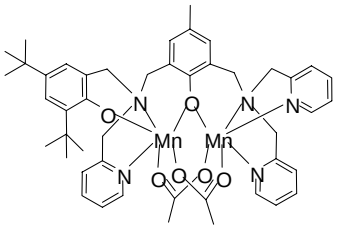
Dinuclear Mn complexes **1**, **2** and **3** in varying oxidation states were subjected to X- and Q-band EPR studies. The oxidation states of **1**, **2** and **3** are at the Mn2(II,II), Mn2(II,III) and Mn2(III,III) states respectively, associated with the increasing O/N ratio in the first ligand sphere. For each complex, several oxidation states are accessible either via bulk electrolysis, e.g. in **2** the II,II and III,III states, or via photoinduced oxidation in the presence of $Ru(II)(bpy)_3$ as the photo-sensitizer and an external electron acceptor pentaaminechlorocobalt(III), to obtain the III,IV state in **2**.

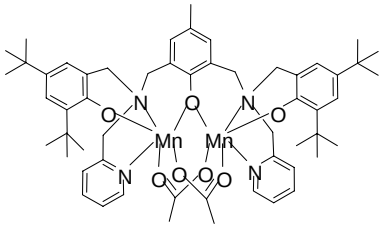
EPR spectral parameters such as *g*- and A-tensors are extracted from simulation and are fitted simultaneously to both X- and Q-band spectra. The variations of the hyperfine coupling constants at different oxidation states are compared for each complex. The association between the different ligand spheres and structural changes occurring upon oxidation to higher valence states and the g- and A-tensors is discussed.



1



2



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References: [1] Huang, P. et. al. *J. Inorg. Biochem.* **2004,** 98, 733-745. [2] Lomoth, R. et. al. *Euro. J. Inorg. Chem.*, **2002**, 11, 2965-2974. [3] Huang, P. et. al. *J. Inorg. Biochem.*, **2002**, 91, 159-172. [4] Anderlund, M. et. al. "Characterization of an unsymmetrical di-manganese complex in different oxidation states" manuscript. [5] Eilers, G. et. al. *Dalton Trans.* **2005**, 6, 1033-1041.

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