A new dinuclear manganese complex ([Mn₂L(µ-OAc)₂]·ClO₄)₂, has been synthesized, where L is the anion of 2-(N,N-Bis(2-methylpyridyl)aminomethyl)-6-(N-(3,5-di-tert-butylbenzyl-2-hydroxy)-N-(pyridylmethyl)aminomethyl)-4-methylphenol. The two coordinated manganese ions are bridged via two bidentate acetate groups and the 4-methylphenolate group of the ligand. Pulsed and cyclic voltammetry, in combination with bulk electrolysis and EPR spectroscopy, revealed that the Mn₂(II,III) complex undergoes three metal-centered, reversible to quasi-reversible processes in dry acetonitrile. The reduction to Mn₂(II,II) at E₁/₂ = -0.53 V vs. Fc⁺/Fc⁰ and oxidation to the Mn₂(III,III) state at E₁/₂ = 0.38 V, are both fully reversible. A second, quasi-reversible oxidation process at E₁/₂ = 0.755 V vs. Fc⁺/Fc⁰ becomes reversible at faster scan rates. The reaction product was short-lived however. As chemical reversibility was obtained for scan rates of ν ≥ 10 Vs⁻¹, a lower limit of the lifetime of the divalent oxidation product of about 100 ms could be estimated. The product of the second oxidation wave could thus not be isolated by bulk electrolysis.

We investigated if a product of 2-electron oxidation could be isolated by flash photolysis by 2 in partly aqueous solution, using Ru(II)-trisbipyridine as photosensitizer and Co(III)-pentaamminechloride as electron acceptor. The EPR spectrum revealed that 2 was then successively oxidized first to Mn₃(III,IV) and then further oxidized to an EPR-silent species. Cyclic voltammetry in solutions with 10% (v:v) water reveal a first oxidation wave peaking at Eₘₐₓ = 0.2 V vs. Fc⁺/Fc⁰ as before. However, the second oxidation appeared already at 0.6V. In addition a third oxidation was observed at ca 0.9 V vs. Fc⁺/Fc⁰. These results indicate that the original complex 2 reacts with water in a way that allows forming higher oxidation states at lower redox potentials than in dry acetonitrile. Implications for structural changes are discussed.

Synthesis and chrystal structure characterization are presented in a separate contribution by Magnus Anderlund et al.