Electronic supplementary information

The role of carboxylato ligand dissociation in the oxidation of chrysin with H₂O₂ catalysed by [Mn_{II,IV}(µ-CH₃COO)(µ-O)₂(Me₄dtne)](PF₆)₂


FTIR spectroelectrochemistry in acetonitrile

A thin-layer IR spectroelectrochemical cell with a CaF₂ window was used for in situ FTIR and electrochemical measurements. Fig. S1 shows changes that occur in the FTIR spectrum of 1 in CD₃CN (0.1 KPF₆) upon oxidation and subsequent reduction and the corresponding differential FTIR spectra with the reference spectrum that recorded while scanning between, nominally, at 0.5-0.7 V vs a Ag wire reference electrode. The changes observed upon oxidation were reversed upon subsequent reduction (the lack of complete reversibility is due to diffusion of oxidised material away from the electrode but still within the IR beam). These data are in agreement with changes observed by UV/vis absorption spectroelectrochemistry in CH₂CN (0.1 M TBAPF₆) and indicate the formation of 2 (i.e. the spectrum obtained matched that of the independently prepared complex 2 in solid state) and the recovery of the spectrum of 1 upon reduction. Fig. S2 compares the differential solid state FTIR spectra (between complex 2 and complex 1) and the differential spectrum obtained in solution upon oxidation. The correspondence between the spectra is excellent, with the minor shifts expected when comparing solid state and solution spectra.

Fig. S1. In-situ FTIR spectroelectrochemistry 1 (5 mM) in 0.1 M KPF₆ - CD₃CN solution (left) and difference spectra (right). The spectra were obtained during one cycle of a cyclic voltammogram at 0.01 mV s⁻¹. The ranges indicate the potential scanned during acquisition of each spectrum in order from top to bottom. Spectra were obtained using an OTTLE cell equipped with CaF₂ windows, platinum counter and working electrodes and a Ag wire reference electrode.
Cyclic voltammetry of $[\text{Mn}_{2}^{III,IV}(\mu-\text{CF}_3\text{CO}_2)(\mu-\text{O})_2(\text{Me}_4\text{dtne})](\text{PF}_6)_2$

The complex $[\text{Mn}_{2}^{III,IV}(\mu-\text{CF}_3\text{CO}_2)(\mu-\text{O})_2(\text{Me}_4\text{dtne})](\text{PF}_6)_2$ was prepared (see experimental section) for comparison with the electrochemical data obtained upon addition of CF$_3$CO$_2$H to acetonitrile solutions of 1. The data confirm that exchange of the carboxylato bridging ligand takes place in solution.

ESI-MS spectroscopy of complex 1 in water

The observed non-innocence of carbonates (originating from air and by deliberate addition) in the speciation of the complex 1 in water was demonstrated by cyclic voltammetry and UV/Vis absorption spectroscopy, which indicated that carbonate exchanges with acetate as a bridging ligand both at pH 6 and 11. Measurement of the ESI-MS spectra would be anticipated to provide
information as to the species present in solution at pH 6 and pH 11, however, the effect of dilution and the conditions of the electrospray require that caution is interpreted in drawing such conclusions, especially given the potential for carbonate to act as a ligand in place of acetate. As pointed out at endnote 25 of the manuscript, ESI-MS was employed in the present study in an effort to gain more information as to the species formed from complex 1 at pH 6 and pH 11.

However, the limitations of this method precludes that its use to make definitive statements as to the species present in solution. Indeed, the dilution of samples prior to analysis shifts equilibria substantially especially where species such as carbonate and acetate vary in concentration also. Nevertheless, the spectra obtained can be assigned relatively straightforwardly if these caveats are borne in mind. Fig S4 shows the ESI-MS spectra of a solution of complex 1 at pH 6 and 11. The peaks at m/z 688, 542, 271.5 m/z are assignable to \([\text{Mn}_{2}^{3+} \text{III,IV}(\mu-HCO_3)(\mu-O)_2(\text{Me}_4dtnel})\text{PF}_6]^+\), \([\text{Mn}_{2}^{3+} \text{III,IV}(\mu-CO_3)(\mu-O)_2(\text{Me}_4dtnel})]^+\), \([\text{Mn}_{2}^{3+} \text{III,IV}(\mu-HCO_3)(\mu-O)_2(\text{Me}_4dtnel})]^2+\), respectively. Although, these data are not necessarily representative of the speciation of the complex in the original solution they confirm the effects observed by cyclic voltammetry and UV/vis absorption spectroscopy in regard to the exchange of the acetate bridge with carbonate.
Fig S4. ESI-MS of the complex 1 (10 µM) in water/tBuOH mixture at pH= 6 (upper spectra), at pH= 11 (lower spectra).
**Resonance Raman and UV/Vis absorption spectroscopy of complex 1 at pH 6 and 11 and the effect of carbonate addition**

The Raman spectra of complex 1 (1 mM) were recorded at pH = 6, 11 at $\lambda_{\text{exc}}$ 355nm. The Raman spectrum at pH 11 shows distinct differences with that at pH 6 in particular with the disappearance of the band at 692 cm$^{-1}$. The UV/Vis absorption spectra at pH 6 and pH 11 differ as expected (see main text). Addition of saturated carbonate solution (at pH 11) to 1 at pH 11 results in a change in the absorption spectrum to resemble more closely that of 1 at pH 6 and the reappearance of a band at 686 cm$^{-1}$, consistent with the formation of a carbonate bridged complex.

Fig. S5. (left) Raman spectra at 355 nm of a) 1 (1 mM) at pH 6, b) 1 (1 mM) at pH 11, c) 1 (1 mM) at pH 11 with 0.1 M carbonate and (right) UV/Vis absorption spectra (right) of the same solutions of 1 (1mM) at pH 6 (red), pH 11, (black), pH 11 with 0.1 M carbonate (green). Contributions to the Raman spectra from quartz and water have been removed by scaled spectral subtraction.
Catalysis of the oxidation of chrysin by 1 with H2O2 in the absence and presence of carbonate.

Fig. S6. Changes in absorption of chrysin (40 µM) at pH 11 after addition of H2O2 (400 µM) and 1 (1 µM) in the absence (red) and presence (blue) of 0.1 M sodium bicarbonate over 15 min.