The role of Sc3+ in the activation of [Mn2IV(µ-O)3(TMTACN)2](PF6)2·H2O in the catalytic oxidation of alkenes with H2O2

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The enhancement of the catalytic activity by addition of redox-inactive metal ions has been noted extensively in reactions as diverse as oxidative dimerisations,[1] reduction of O2,[2] Wacker-type oxidations,[3] and hydroxylations.[4] In particular, the effect of Lewis acids on the reactivity of Fe(IV)=O species has been studied experimentally and computationally.[5,6] Recently, Lewis acids such as Sc3+ have been reported to enhance the activity of the alkene oxidation catalyst [Mn3(µ-O)3(tmtacn)2]2+,[7,8] which prompted us to investigate the origin of the effects noted. Here, spectroscopic, electrochemical, and DFT studies by our groups will be discussed, and especially the effect of Sc(OTf)3 on the catalyst’s reduction potential and spectroscopic properties. We show that Sc3+ acts similar to proton sources,[9] primarily in the accelerated reduction to form the active species, but plays little role in the catalytic cycle itself.

Raman spectra of the catalyst before and after addition of two equivalents of scandium triflate in acetonitrile.