Dioxygen activation with Co(II) complexes with nitro-substituted ligands

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Dioxygen activation in cobalt complexes has been well studied and uses for the phenomenon have been found in several different fields such as biomimetics,1 transport and storage of oxygen and catalytic oxidation of organic substrates.2 The mechanism of uptake of molecular oxygen by cobalt complexes has been extensively studied and it has been suggested that O2 may undergo a one electron reduction to form a superoxide radical which quickly reacts with another cobalt site to form a peroxo dimer.3 In this study we have investigated the oxidation of Co(II) to Co(III) via dioxygen activation. Our structural and spectroscopic studies suggest that in the binding process two Co(II) ions are oxidized to Co(III) and aerial O2 is reduced to peroxide. It was possible to isolate and characterize a metastable peroxo Co(III) dimer intermediate which is stable at room temperature in the solid state when removed from the mother liquor, Figure 1. We have also studied the formation of the dimer using EPR spectroscopy which suggests the formation of a short-lived superoxide intermediate, Figure 2.

Figure 1: Crystal structure of Co(III) peroxo dimer

Figure 2: EPR spectrum of reaction mixture at 78K