

Oxygen activation by Co(II) and V(IV) complexes with 3,7-diazabicyclo[3.3.1]nonane-derived ligands

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The rigid diazabicyclo[3.3.1]nonane (bispidine) backbone is preorganized for a variety of transition metal ions. The variation of the denticity and type of donor groups allows to tune the metal ion selectivity. The Fe(II) bispidine / hydrogenperoxide system has been shown to be an efficient oxidation catalyst. In order to understand the reaction mechanism and to search for similar reactivities with other metal ions, we have investigated Co(II) and V(IV) bispidine systems.

Co(II) complexes with tetra- and pentadentate bispidine ligands are remarkably inert in air, their oxidation was only possible with hydrogen peroxide. The metal-donor distances in the Co(III) complexes are very short and induce strain to the ligand; the corresponding Co(II) ions are known to fit well into the ligand cavity. Oxidation of the Co(II) complex of a tetradentate bispidine ligand leads to an unusual demethylation and reasons for this ligand-based reaction and possible mechanisms and implications for catalytic oxidation reactions are discussed.

Structural and spectroscopic data of vanadyl(IV) complexes of tetra- and pentadentate bispidine ligands are presented. The kinetics of the oxidation of these complexes with hydrogen peroxide and structural and spectroscopic data of the products is presented. Of particular interest is a V(V)-oxo-peroxo complex with a pentadentate bispidine ligand with side-on coordination of a peroxo group. The observed O-O bond is unusually short. Further oxidation of this complex with Ce(IV) is also described.

