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Synthesis and molecular structure of manganese complexes with hindered N_3 ligand

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Manganese-dioxygen complexes are assumed to play significant roles in physiologically important enzymatic reactions including superoxide dismutation, decomposition of hydrogen peroxide and dioxygen evolution from water catalysed by manganese containing proteins [1]. Accordingly, the characterization of structurally well-defined manganese-dioxygen complexes are important from bioinorganic viewpoints. Here, we report the synthesis and molecular structure of manganese(II)-chloro, hydroxo, manganese(III)-oxo complexes of the hydro*tris*(3,5-diisopropyl-1-pyrazolyl)borate ligand and oxidation behaviour of the Mn(II)-hydroxo complexes. When *bis*(μ-hydroxo)-dimanganese(II,II) complex was reacted with excess amount of H_2O_2 in the presence of 3,5-diisopropylpyrazole (3,5-$^{i}Pr_2$pzH) (2 equiv.) at room temperature for 30 min, a colour change was observed and the resultant complex was found to be the intramolecular hydrogen bonded peroxo complex Mn(O_2)(3,5-$^{i}Pr_2$pzH)(HB(3,5-$^{i}Pr_2$pz)$_3$). This complex is not stable and decomposes slowly in solution at room temperature. The reaction of a *bis*(μ-oxo)dimanganese(III,III) with excess amount of H_2O_2 in the presence of 2-methylimidazole (2-MeIM) resulted in the isolation of intermolecular hydrogen bonded monomeric side-on peroxo manganese(III) complex, Mn(O_2)(2-MeIM)(HB(3,5-$^{i}Pr_2$pz)$_3$). The O–N distances in this complex are shorter (011-N82, 2·76(1) Å) than the range of distances expected for a hydrogen bond between the peroxide and the imidazole proton. The complex is stable at room temperature and is unable to oxidize triphenylphosphine and ethyl vinyl ether.

Reference

1. Pecoraro V L, Baldwin M J and Gelasco A 1994 *Chem. Rev*. **94** 807