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Vanadium(V) complexes of some bidentate hydrazone ligands and their bromoperoxidase activity

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Abstract

Dinuclear methoxy bridged complexes of vanadium, $[\text{VO}(\mu\text{-OMe})(\text{OMe})(\text{L})]_2$ (**1-3**) have been synthesized from the reaction of $\text{VOSO}_4 \cdot \text{H}_2\text{O}$ with triethylamine and the respective hydrazone ligand. The compounds have been characterized by spectroscopic methods and determination of single crystal X-ray structure of one of them (**1**). DFT and TD-DFT calculations were used to understand the electronic structures of the complexes and their electronic spectra respectively. Though the dimeric complexes are stable in the solid state, the ESI-MS spectra as well as ^1H -NMR spectra of the complexes suggest that in solution the monomeric forms of the complexes are the major species. The V(V) complexes in DMF were used to catalyze the oxidative bromination of salicylaldehyde, in aqueous $\text{H}_2\text{O}_2/\text{KBr}$ in the presence of HClO_4 at room temperature. The complexes show exceptionally high bromoperoxidase activity with salicylaldehyde as a model substrate to produce 5-Bromo salicylaldehyde in good yield and high TOF and TON. Therefore, these complexes behave as functional models of vanadate dependent bromoperoxidase enzyme.

Keywords: Vanadium (V), hydrazone, methoxy ligand, bromoperoxidase activity, DFT calculations

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