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Vanadium (V) Complexes of a Tripodal Ligand, Their Characterization and Biological Implications

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Abstract : The reaction of the tripodal tetradentate dibasic ligand 6,6'–(2–(pyridin–2–yl)ethylazanediyl)bis(methylene)bis(2,4–di–tert–butylphenol), H2L1 I, with [VIVO(acac)2] in CH3CN gives the VVO–complex, [VVO(acac)(L1)] 1. Crystallization of 1 in CH3CN at ~0 ºC, gives dark blue crystals of 1, while at room temperature it affords dark green crystals of [{VVO(L1)}2µ–O] 3. Upon prolonged treatment of 1 in MeOH [VVO(OMe)(MeOH)(L1)] 2 is obtained. All three complexes are analyzed by single–crystal X–ray diffraction, depicting distorted octahedral geometry around vanadium. In the reaction of H2L1 with VIVOSO4 partial hydrolysis of the tripodal ligand results in elimination of the pyridyl fragment of L1 and the formation of H[VVO2(L2)] 4, containing the ONO tridentate ligand 6,6'–azanediylbis(methylene)bis(2,4–di–tert–butylphenol), H2L2 II. Compound 4, which was not fully characterized, undergoes dimerization in acetone yielding the hydroxido–bridged [{VVO(L2)}2µ–(HO)2] 5, having distorted octahedral geometry around each vanadium. In contrast, from a solution of 4 in acetonitrile, the dinuclear compound [{VVO(L2)}2µ–O] 6 is obtained, with trigonal bipyramidal geometry around each vanadium. The methoxido complex 2 is successfully employed as a functional catechol–oxidase mimic in the oxidation of catechol to o–quinone under air. The process is confirmed to follow a Michaelis–Menten type kinetics with respect to catechol, the Vmax and KM values obtained being 7.66×10–6 M min -1 and 0.0557 M, respectively, and the turnover frequency is 0.0541 min–1. Complex 2 is also used as a catalyst precursor for the oxidative bromination of thymol in aqueous medium. The selectivity shows quite interesting trends, namely when not using excess of primary oxidizing agent, H2O2 the para mono–brominated product corresponds to ~93 % of the products and no dibromo derivative is formed.

Keywords : oxidovanadium (V) complexes, tripodal ligand, crystal structure, catechol oxidase mimetic activity
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