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# Copper(II) complexes of a polydentate imidazole-based ligand. pH effect on magnetic coupling and catecholase activity

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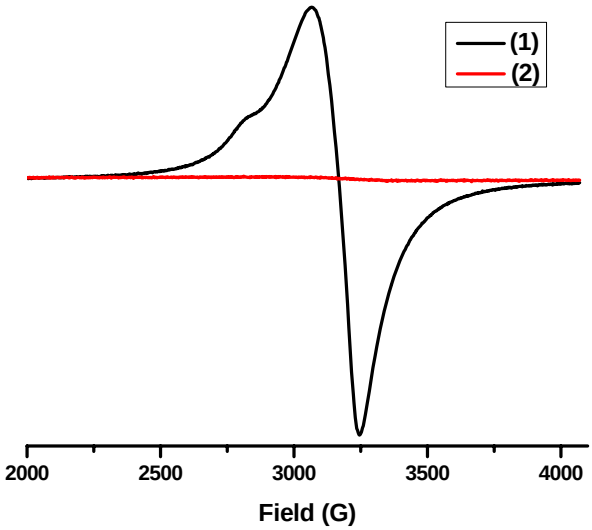


**Figure S1.** Powder EPR spectra at room temperature of the complexes (Black) **1**, $[Cu_4(H_2$*Valbiim*$)(H_2O)_{10}](BF_4)_4 \bullet 6H_2O$ and (Red) **2**, $[Cu_4($*Valbiim*$)(\mu\text{-}OH)_2(H_2O)_4] \bullet 5H_2O$

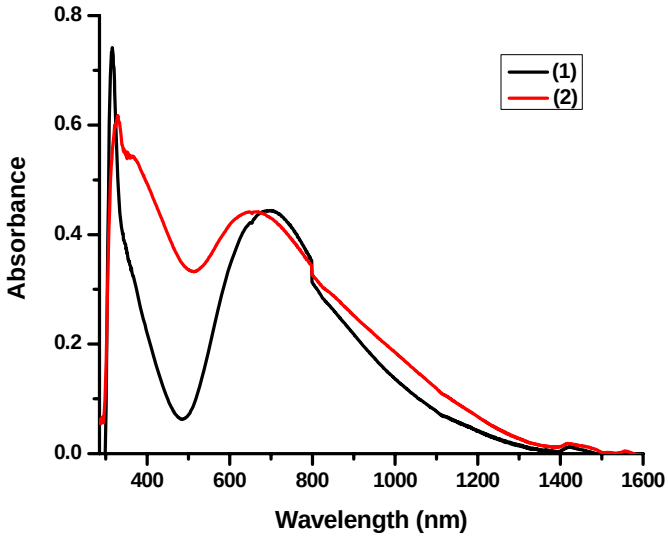


**Figure S2.** Diffuse reflectance spectra of the complexes (Black) **1**, $[Cu_4(H_2$*Valbiim*$)(H_2O)_{10}](BF_4)_4 \bullet 6H_2O$ and (Red) **2**, $[Cu_4($*Valbiim*$)(\mu\text{-}OH)_2(H_2O)_4] \bullet 5H_2O$ The abnormality near 800 nm is due to change of detector.

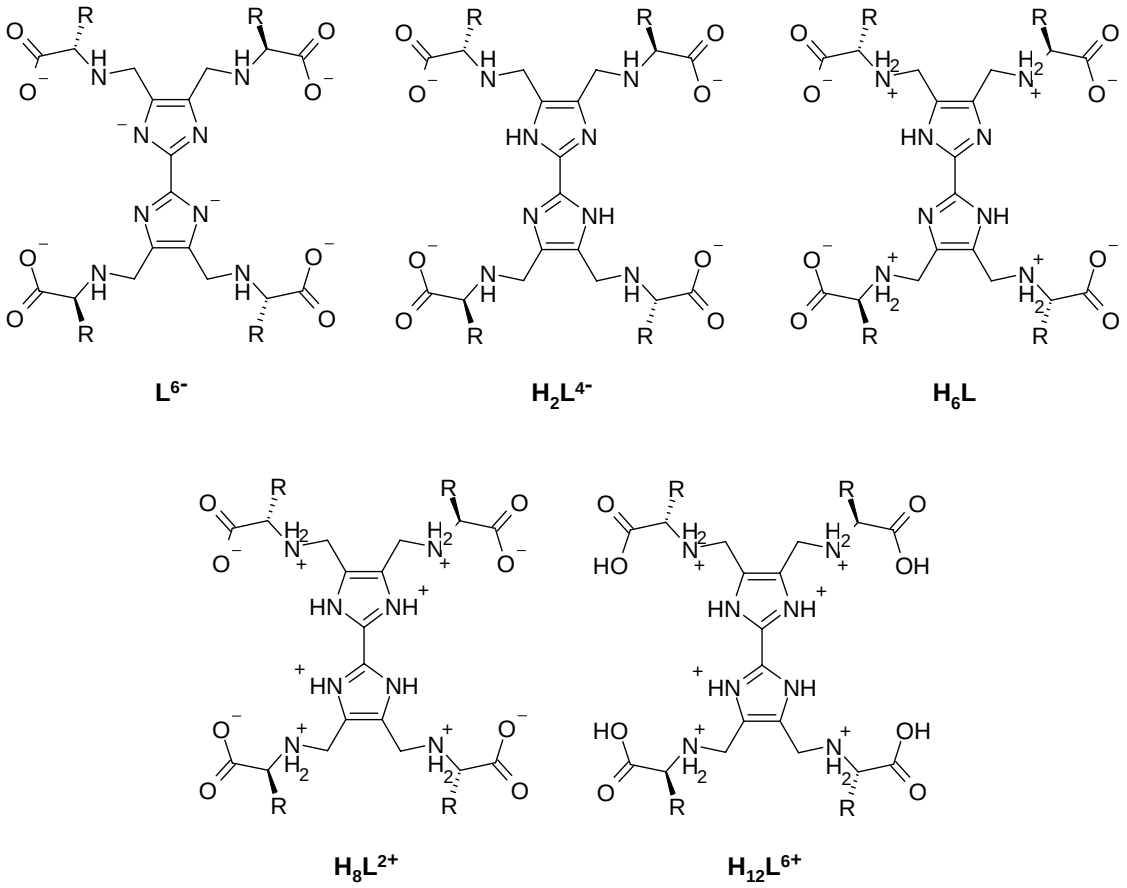


**Figure S3.** Some of the different possible protonation degrees of the ligand $H_6$*Valbiim*.

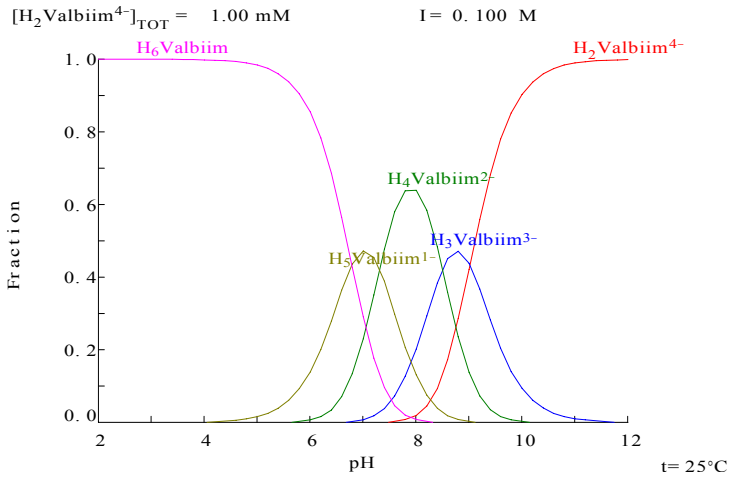


**Figure S4.** Species distribution diagram as a function of pH for $H_6$*Valbiim* in aqueous solution.

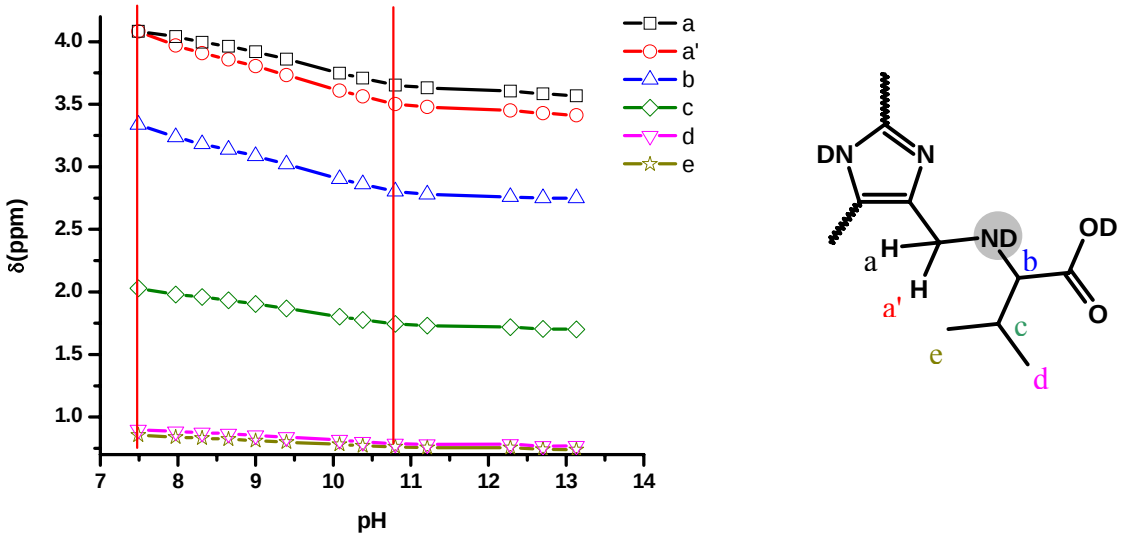


**Figure S5.** Changes in chemical shifts of selected $^{1}$HNMR signals of $H_6$*Valbiim* as function of the pH.

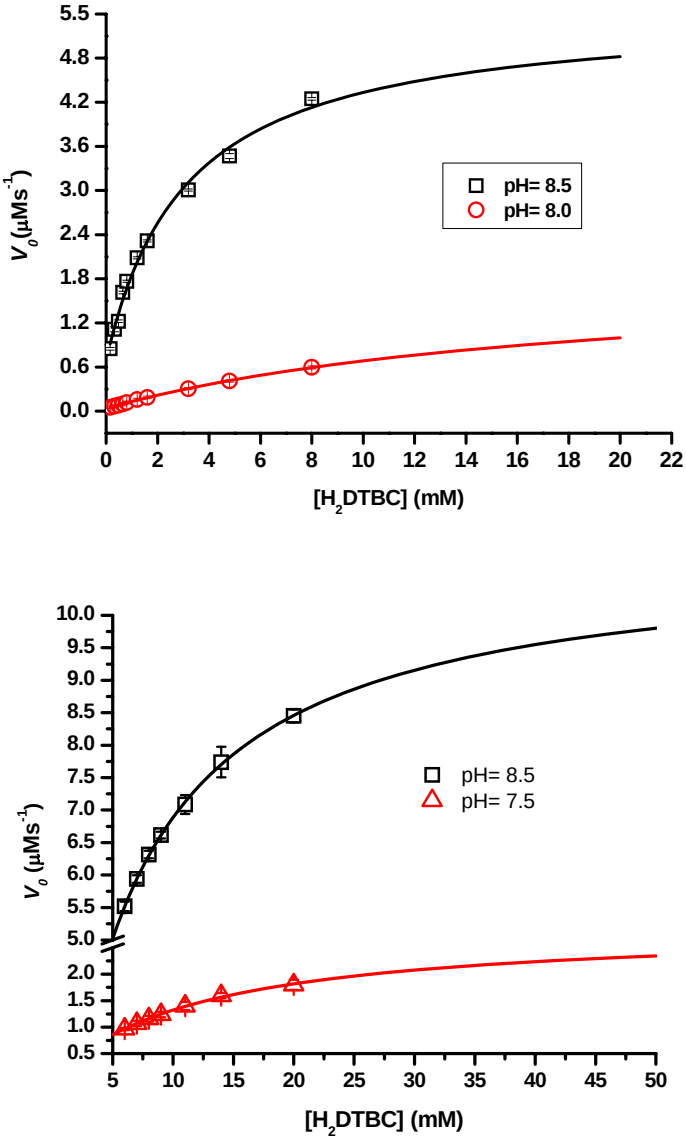


**Figure S6.** Dependence of the reaction rates on the $H_2$DTBC concentrations for the oxidation catalyzed by $Cu_4$Valbiim in (up) MeOH/$H_2O$ and (down) MeCN/$H_2O$.

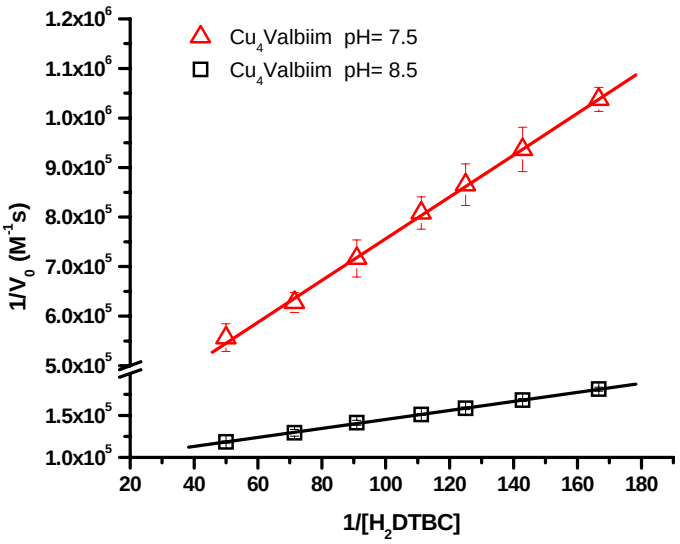


**Figure S7.** Lineweaver-Burk plot for aerobic oxidation of $H_2$DTBC by complex $Cu_4$*Valbiim* in MeCN/$H_2O$.

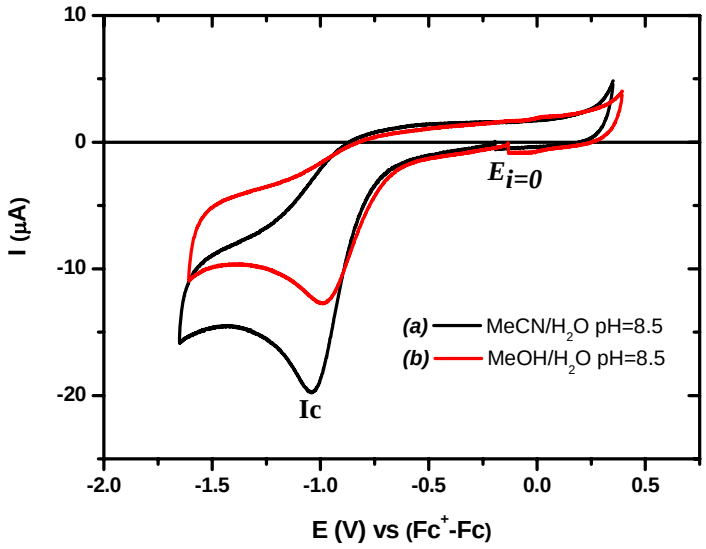


**Figure S8.** Cyclic voltammograms of atmospheric $O_2$ saturated solutions of 0.1 M HEPES pH = 8.5 in MeCN/$H_2O$; 1:1 (black line) and MeOH/$H_2O$; 1:1 (red line) at 78.1 KPa. Scan rate 0.1 $Vs^{-1}$. Vitreous carbon disk (7.1$mm^2$). Ag/AgBr, 0.1 M $Bu_4NBr$ reference electrode.

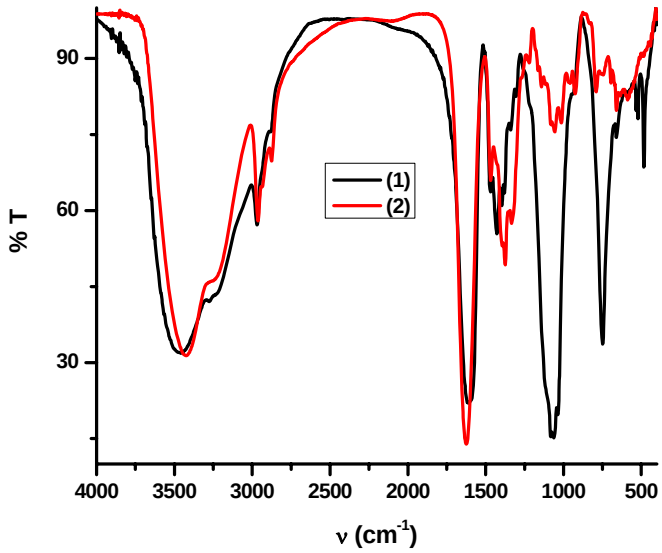


**Figure S9.** IR spectra of the complexes (Black) **1**, $[Cu_4(H_2Valbiim)(H_2O)_{10}](BF_4)_4 \bullet 6H_2O$ and (Red) **2**, $[Cu_4(Valbiim)(\mu\text{-}OH)_2(H_2O)_4] \bullet 5H_2O$ in KBr pellet.

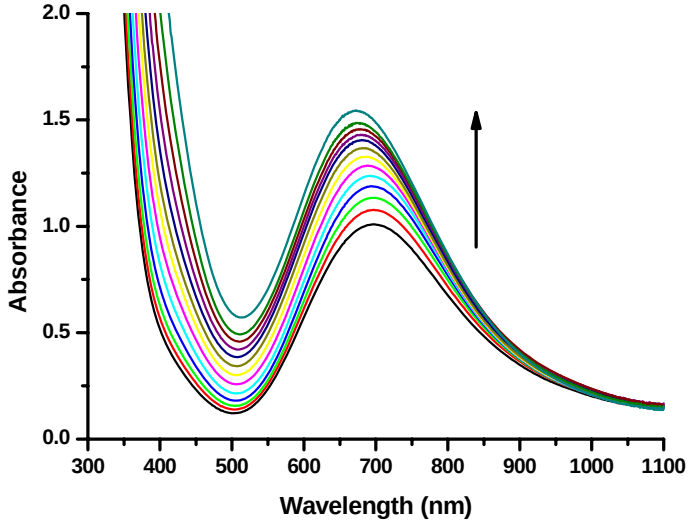


**Figure S10.** UV-Vis spectra of $[Cu_4Valbiim]$ (5 mM) in methanol solution at 25 °C as a function of $NBu_4OH$ added. The first line is the spectrum of a solution $4Cu{:}H_6Valbiim$ and the subsequent are the spectra of this solution plus 0.5 to 6 eq.