Electronic supplementary information for

Attila Jancsó, Zoltán Paksi, Noémi Jakab, Béla Gyurcsik, Antal Rockenbauer and Tamás Gajda*

Solution chemical properties and catecholase-like activity of the copper(II)-Ac-His-His-Gly-His-OH system, a relevant functional model for copper containing oxidases

Figure S1. pH dependence of the UV-Vis spectra (A) of the copper(II)–hhgh system ([Cu^{II}] = [hhgh] = 0.7 mM, T = 298 K, I = 0.1 M NaCl, pH = 2.6-11.0), and the individual electronic absorption spectra of the formed species (B).

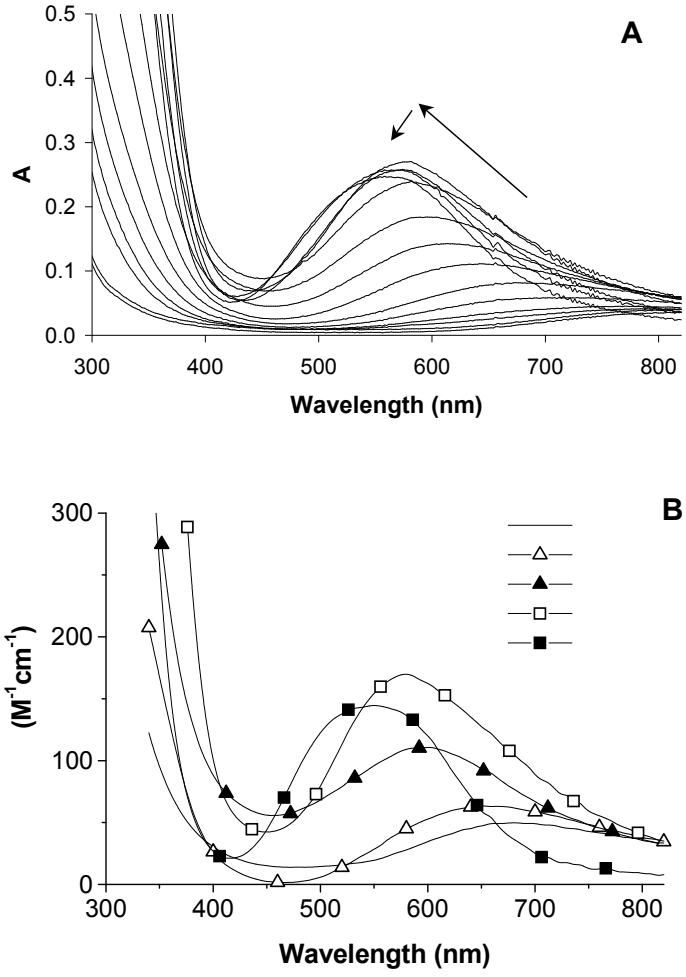

Figure S2. Calculated EPR spectra of the individual species formed in the copper(II)-hhgh system

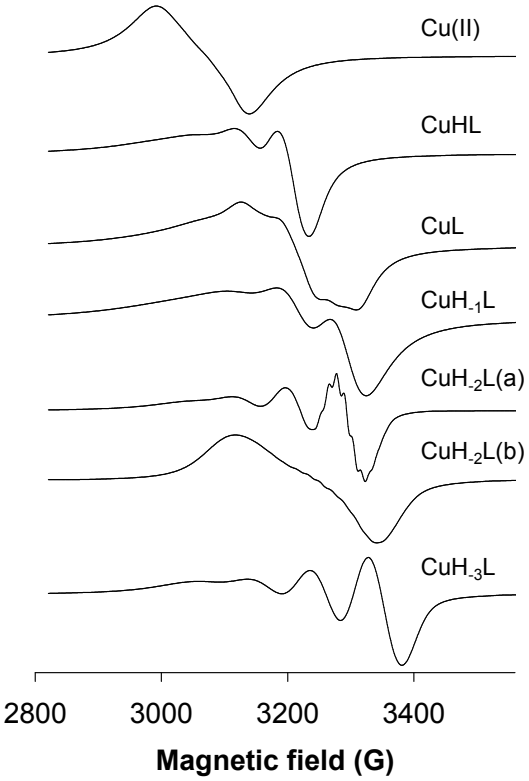

Figure S3: Inhibition of the Nitroblue Tetrazolium (NBT) reduction as a function of the copper(II) concentration in 0.05 M phosphate buffer (□: $[Cu^{2+}]$ = [hhgh], pH = 6.8; ○: $[Cu^{2+}]$ = [hhgh], pH = 7.5; △: $[Cu^{2+}]$ = 0.1[hhgh], pH = 7.5). The inhibition caused by Cu,Zn-SOD is shown in the insert. The following species are present in the solutions:

Cu^{2+} (32%), CuL (35%) and $CuH_{-1}L$ (28%) at pH 6.9 and $[Cu^{2+}]$ = 0.95[hhgh] = 0.2 μM;

Cu^{2+} (10%), CuL (19%), $CuH_{-1}L$ (56%) and $CuH_{-2}L$ (13%) at pH = 7.5 and $[Cu^{2+}]$ = 0.95[hhgh] = 0.2 μM;

CuL (20%), $CuH_{-1}L$ (63%) and $CuH_{-2}L$ (16%) at pH = 7.5 and $[Cu^{2+}]$ = 0.1[hhgh] = 0.2 μM.

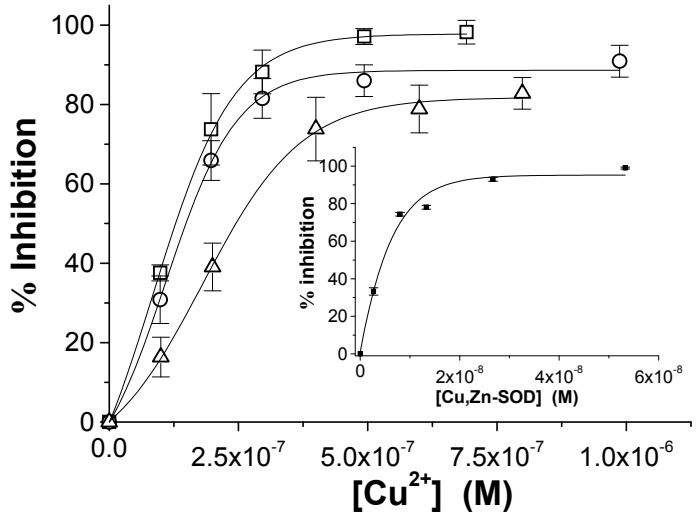

Figure S4. The CD spectra of the copper(II)–hhgh system ([Cu^{II}] = [hhgh] = 0.055 mM, T = 298 K, I = 0.1 M NaCl, pH = 7.8-12.03) at different pH in 86 w% methanol-water solvent mixture. The calculated $\Delta\varepsilon$ values are based on the total metal ion concentration.

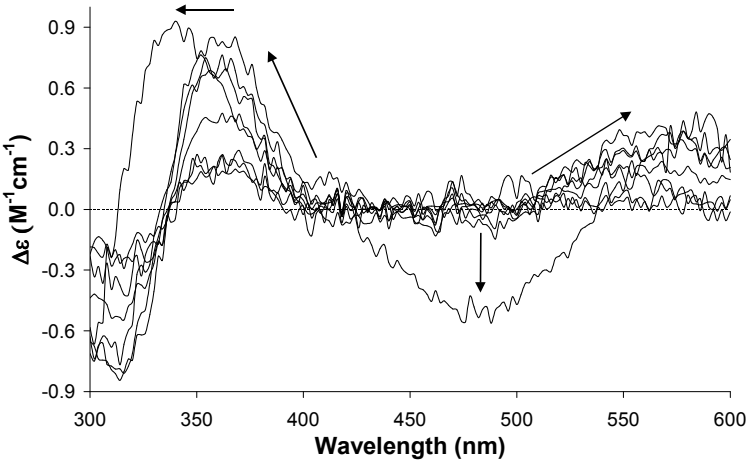

Figure S5. The pH dependence of the average CD intensity between 355 and 365 nm (the maximum detected for the spectrum of the species $CuH_{-2}L$). The solid line was calculated using $pK_1 = (9.6 \pm 0.1)$ and $pK_2 = (11.0 \pm 0.2)$.