

Supporting Information for

Binding models of copper(II) thiosemicarbazone complexes with human serum albumin: a speciation study

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Table S1. EPR parameters of the components obtained in Cu-mim solutions^a

Component	g_x	g_y	g_z	A_x/G	A_y/G	A_z/G	a_x^N/G	a_y^N/G	a_z^N/G	$g_{0,calc}^b$
[CuL] ²⁺	2.051	2.058	2.315	17.2	17.4	149.0	11.0	8.7	10.0	2.1411
[CuL ₂] ²⁺	2.046	2.062	2.288	26.3	18.7	158.9	15.3	15.1	11.0	2.1320
							12.0	15.9	10.0	
[CuL ₃] ²⁺	2.047	2.062	2.284	28.7	20.7	160.5	15.6	15.9	13.3	2.1309
							15.6	15.9	13.3	
							14.5	15.7	7.0	
[CuL ₄] ²⁺	2.049	2.050	2.253	18.0	19.3	182.9	14.0	16.3	13.3	2.1174
							14.0	16.3	13.3	
							16.9	12.8	7.0	
							16.9	12.8	7.0	

^a The experimental error were ± 0.001 for g , ± 1 G for A and a_N tensor values. ^b Isotropic values of the g tensor were calculated via equation: $g_0 = (g_x + g_y + g_z)/3$.

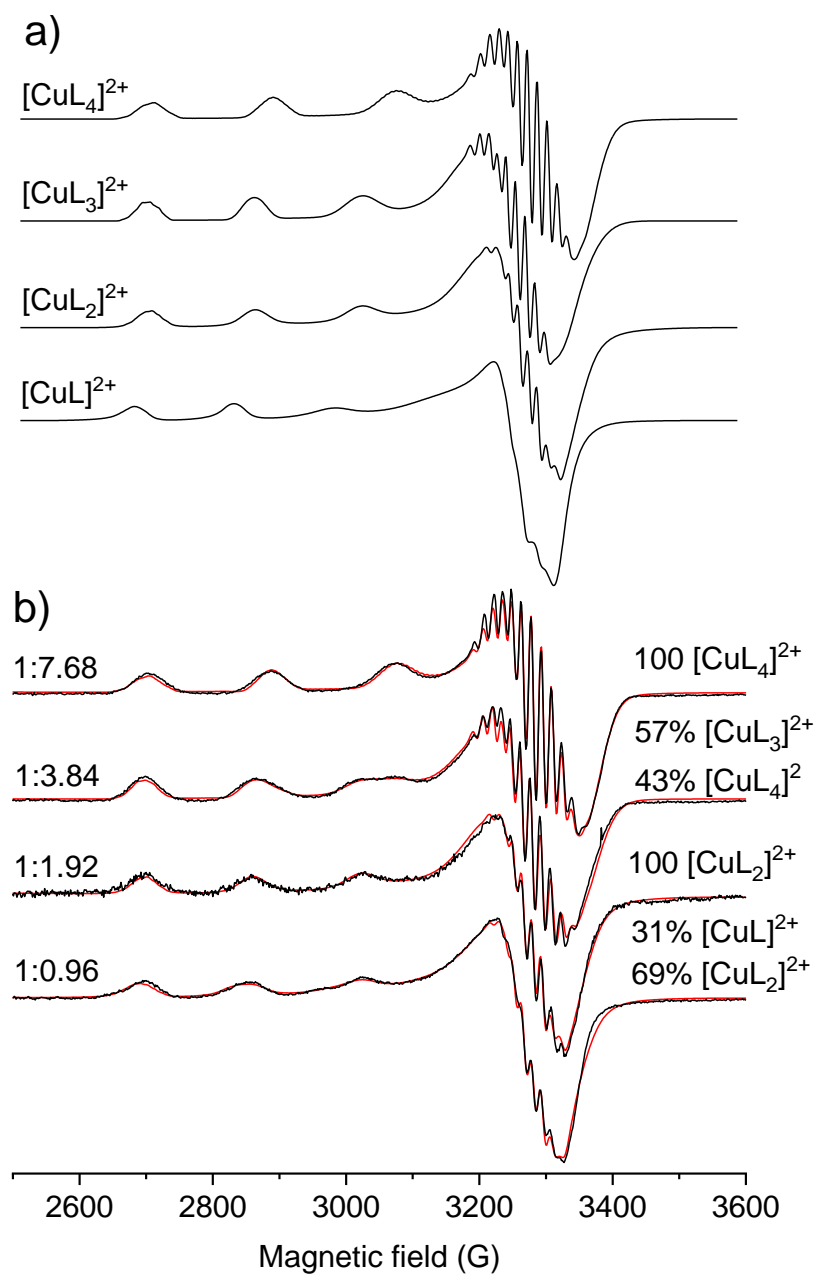


Figure S1. **a)** Simulated EPR spectra calculated for the copper(II) complexes of mim with the parameters given in Table S1. **b)** Measured (black) and calculated (red) frozen solution EPR spectra recorded at $c_{\text{Cu(II)}} = 2.18 \times 10^{-4}$ M, numbers above the spectra indicate the different copper(II) - mim concentration ratios.

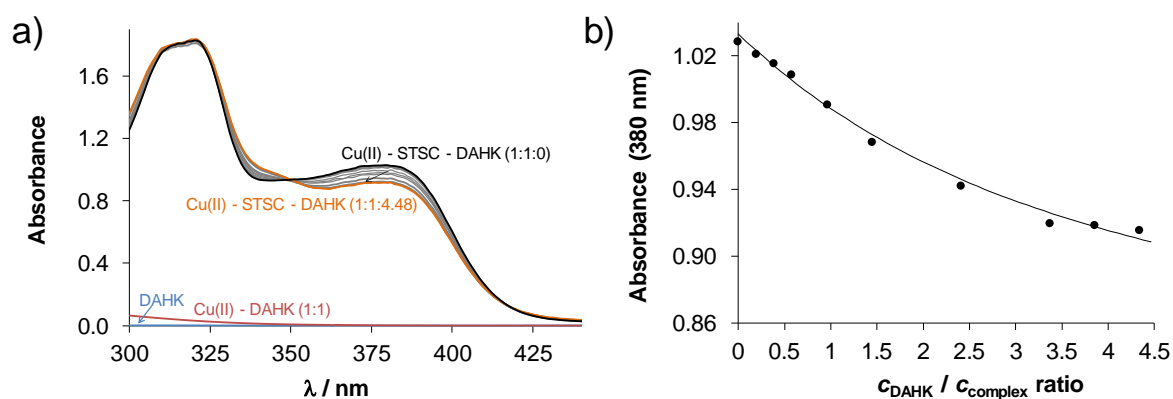


Figure S2. a) UV-vis spectra recorded for the copper(II) – STSC – DAHK (1:1:x) system at pH 7.4 after 4 h equilibration time (x: 0 – 4.5). b) Absorbance values at 380 nm plotted against the ratio of DAHK and the copper(II)-STSC complex). $\{c_{\text{Cu(II)}} = c_{\text{STSC}} = 200 \mu\text{M}, c_{\text{DAHK}} = 0\text{--}896 \mu\text{M}; 30\% \text{ (w/w) DMSO/H}_2\text{O}; \text{pH} = 7.4 \text{ (20 mM HEPES)}; T = 25 \text{ }^\circ\text{C}; I = 0.10 \text{ M (KCl)}; \ell = 0.5 \text{ cm}\}$

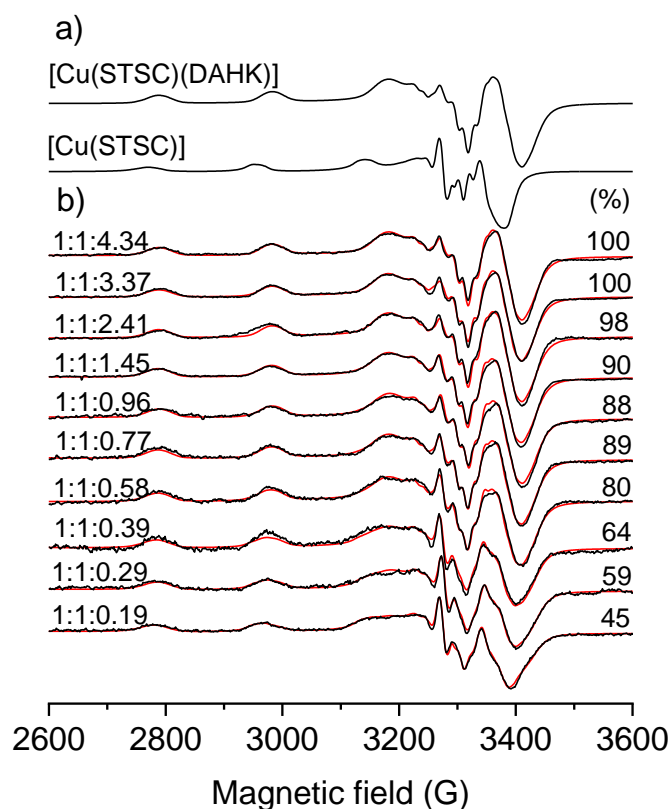


Figure S3. a) Simulated EPR spectra calculated for species formed in the copper(II) – STSC – HSA system with parameters given in Table 2. b) Measured (black) and calculated (red) frozen solution EPR spectra recorded for the same system; numbers above the spectra indicate the different copper(II)-to-STSC-to-DAHK ratios. The ratio (%) refers to the fraction of [Cu(STSC)(DAHK)] component taken into account for the simulation of the spectra.

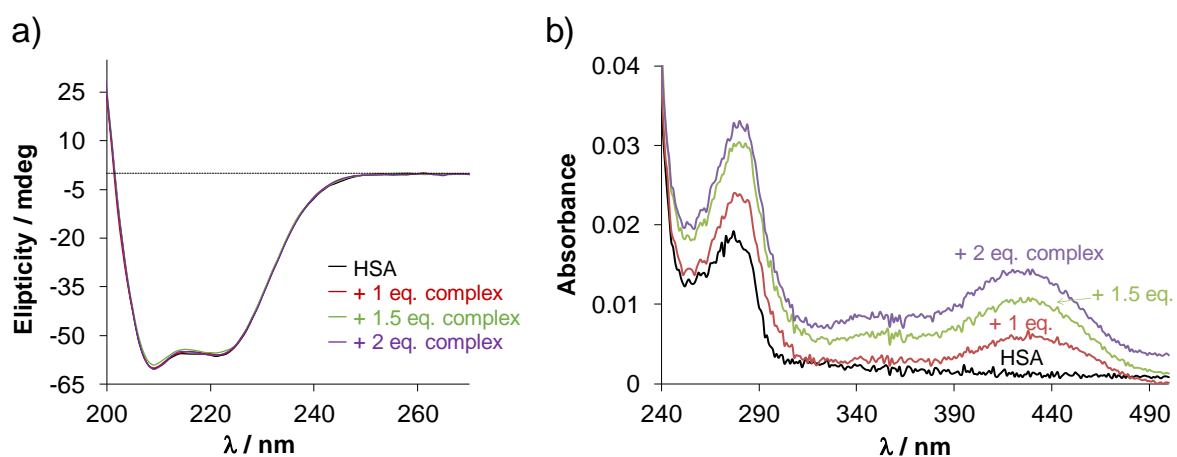
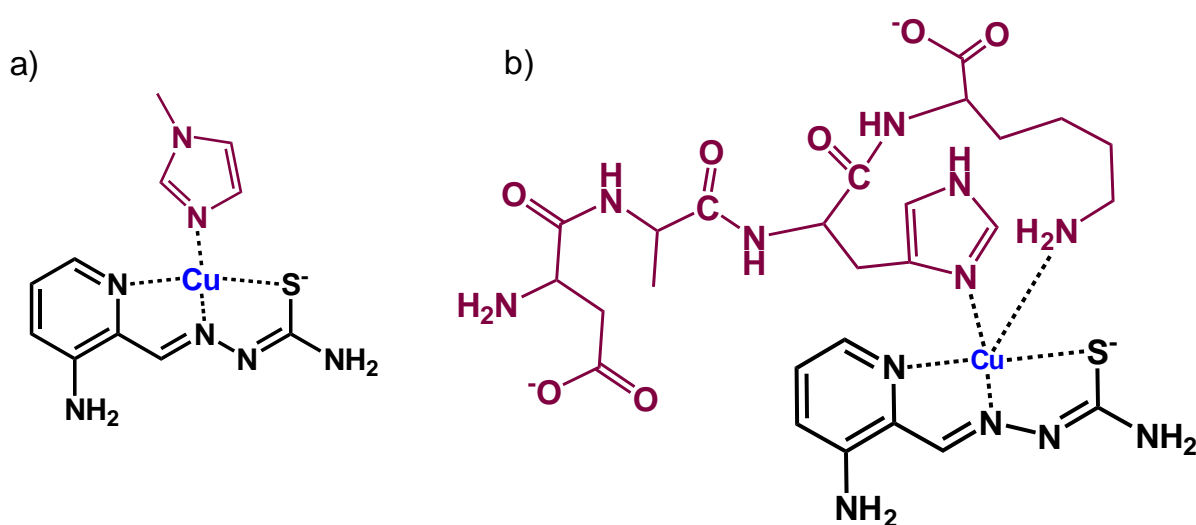


Figure S4. a) Circular dichroism spectra recorded for HSA alone and in the presence of various equivalents of the copper(II)-Triapine complex in pure water at pH 7.4, and b) the corresponding UV-vis spectra. The circular dichroism spectra were recorded on a JASCO J-1500 instrument. $\{c_{\text{HSA}} = 5 \mu\text{M}; T = 25 \text{ }^\circ\text{C}; l = 0.10 \text{ M (KCl)}; \ell = 1 \text{ cm}\}$



Scheme S1. Possible structures for the [CuAL] ternary complexes formed in the a) copper(II) - Triapine - mim and b) copper(II) - Triapine - DAHK systems.