Supplementary Material (ESI) for Dalton Transactions

Supporting Information for:

A Study on the Coordinative Versatility of new N,S-donor Macrocyclic Ligands: XAFS, and Cu^{2+} complexation thermodynamics in solution

Giuliana Aquilanti,[a] Marco Giorgetti,*[b] Marco Minicucci,[c] Grazia Papini,[c] Maura Pellei,[c] Matteo Tegoni,*[d] Andrea Trasatti,[c] and Carlo Santini*[c]

[a] Sincrotrone Trieste S.C.p.A., S.S. 14 Km 163.5, 34149 Basovizza, Trieste, Italy.
[b] Dipartimento di Chimica Fisica ed Inorganica, Università di Bologna.
[c] School of Science and Technology, Università di Camerino, via S. Agostino 1, 62032 Camerino, Macerata, Italy.
[d] Dipartimento di Chimica Generale ed Inorganica, Università di Parma, Viale degli Usberti 17, I 43100 Parma, Italy.

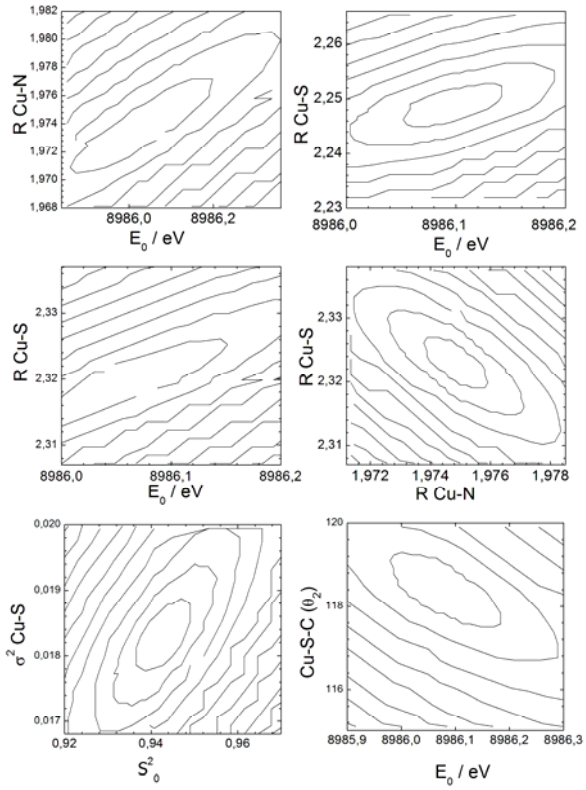

Fig S0 Examples of the two dimensional section of the parameter space (contour plots) for sample **4**. The inner elliptical contour corresponds to the 95% confidence level.

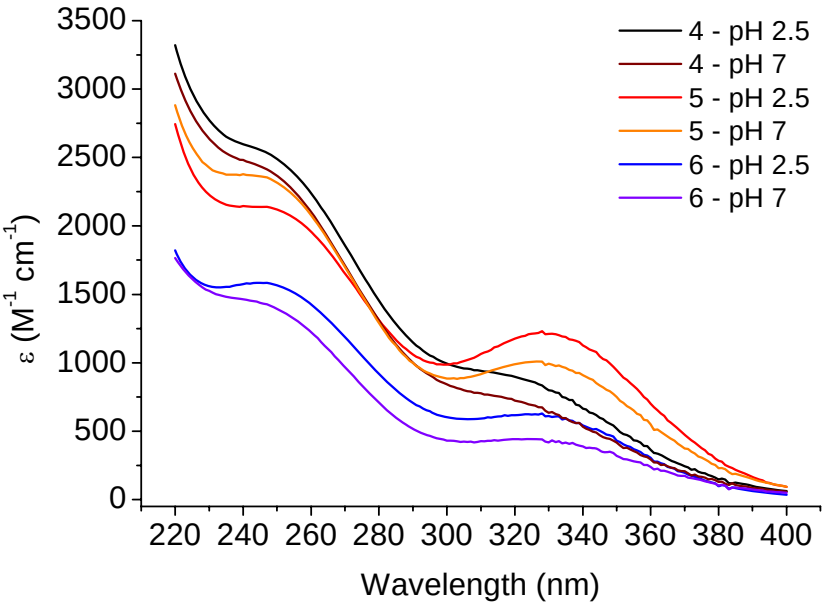

Figure S1. UV spectra of samples containing compounds **4**, **5** and **6** at different pH. C_4 = 6.9 10^{-3} M, C_5 = 5.6 10^{-3} M, C_6 = 7.13 10^{-3} M.

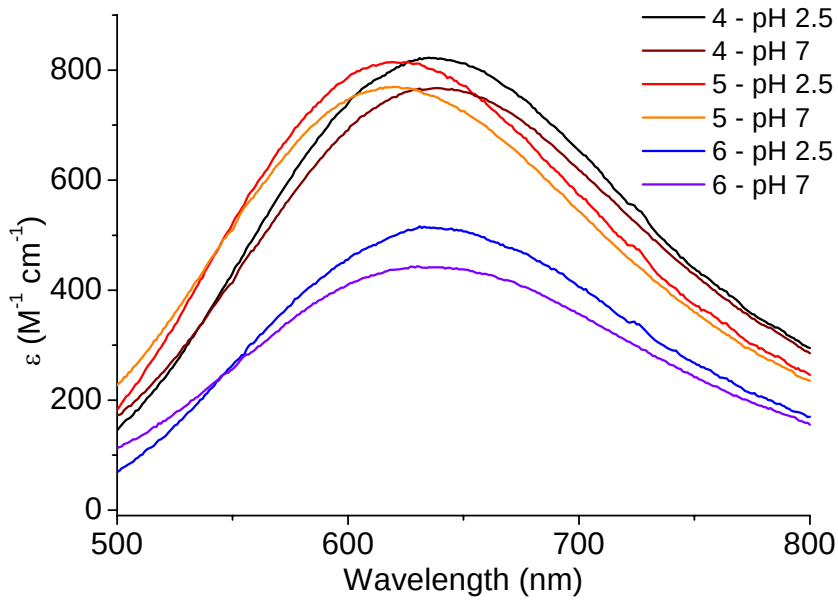

Figure S2. Visible spectra of samples containing compounds **4**, **5** and **6** at different pH. $C_{\mathbf{4}}$ = 6.9 10^{-3} M, $C_{\mathbf{5}}$ = 5.6 10^{-3} M, $C_{\mathbf{6}}$ = 7.13 10^{-3} M.

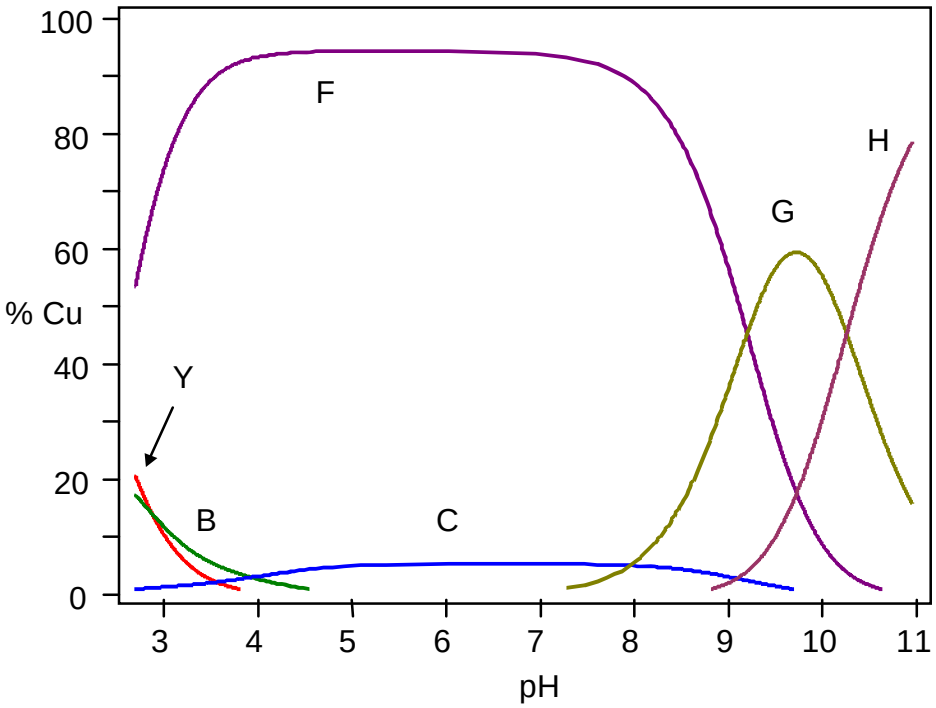

Figure S3. Representative distribution diagram for the system Cu/**1** (L). (Cu:L = 1.9:1, C_{Cu} = 2.2 10^{-3} M). Y: Cu^{2+}; B: $[Cu(H_2L)]^{2+}$; C: $[Cu(HL)]^{+}$; F: $[Cu_2L]^{2+}$; G: $[Cu_2L(OH)]^{+}$; H: $[Cu_2L(OH)_2]$. Labelling was made consistent with that in figure 1 (see text) for simplicity.

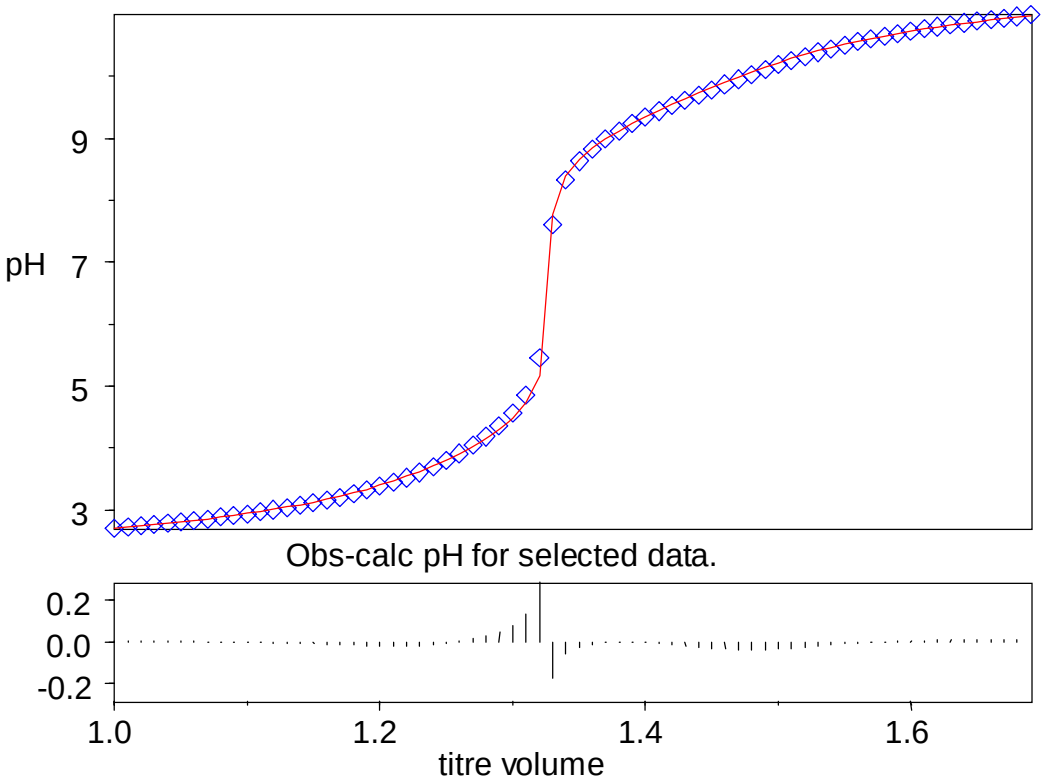

Figure S4. Representative titration curve for the Cu/**1** (L). (Cu:L = 1:1.05, C_{Cu} = 1.22 10^{-3} M). Blue diamonds: experimental pH values; red dotted line: calculated pH values.

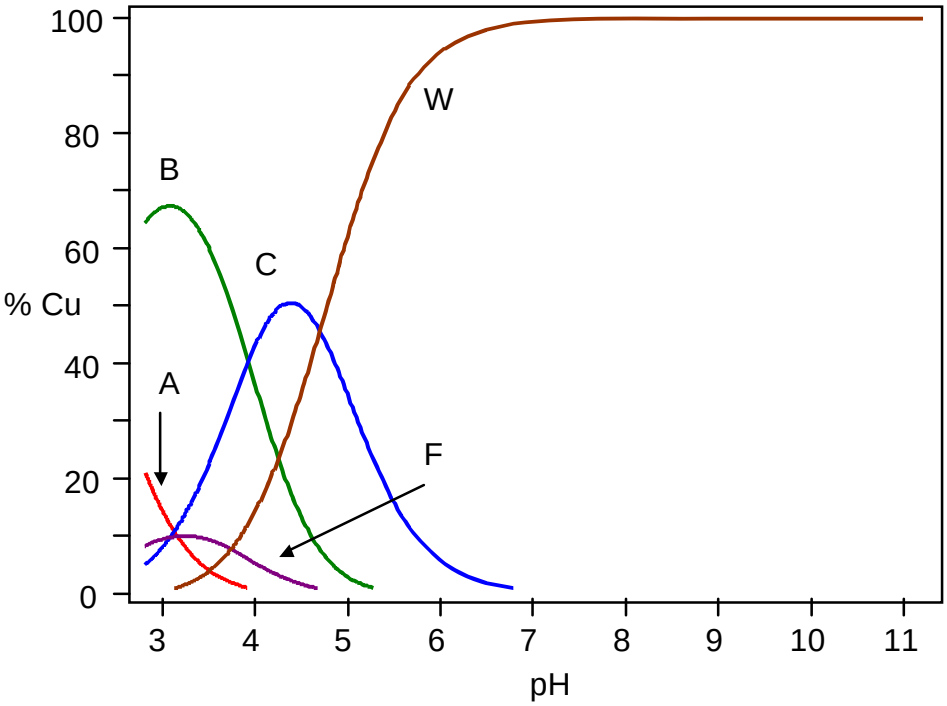

Figure S5. Representative distribution diagram for the system Cu/**1** (L). (Cu/L/Trien = 1:1.05:1.02, C_{Cu} = 1.1 10^{-3} M). A: $[Cu(H_3L)]^{3+}$; B: $[Cu(H_2L)]^{2+}$; C: $[Cu(HL)]^{+}$; F: $[Cu_2L]^{2+}$; W: $[Cu(Trien)]^{2+}$. Labelling was made consistent with that in figure 1 for simplicity.

It is well known from the literature that when metal complexation occurs at low pH and it is not pH dependent, it is possible to determine by pH-metry only the successive pK_a values for the deprotonation processes involving the species [$CuLH_n$], but not the overall formation constant values for the complex species [F. J. C. Rossotti, *The Determination of Stability Constants*, McGraw-Hill Book Co., Inc., New York, **1961**; b) M. T. Beck, I. Nagypal, *Chemistry of Complex Equilibria*, Horwood, Halsted Press, New York, **1990**]. The reason is that the Cu^{2+} + LH_n= [$CuLH_n$] equilibria is not protolytic and cannot be studied by pH-metry. This problem can be however overcome by the use of a suitable competing ligand capable to form metal complexes through a protolytic equilibria. This additional ligand competes with the ligand of interest for Cu^{2+} complexation in certain ranges of pH: the amount of Cu^{2+} bound to the competing ligand is then correlated to the stability constant of the Cu^{2+} complexes with the first ligand. This laboratory have already used this strategy in the past using for instance EDTA as competing ligand for the study of the formation of strong copper(II)-aminohydroxamate ligands [F. Dallavalle, G. Folesani, A. Sabatini, M. Tegoni, A. Vacca, *Polyhedron* **2001**, *20*, 103-109].

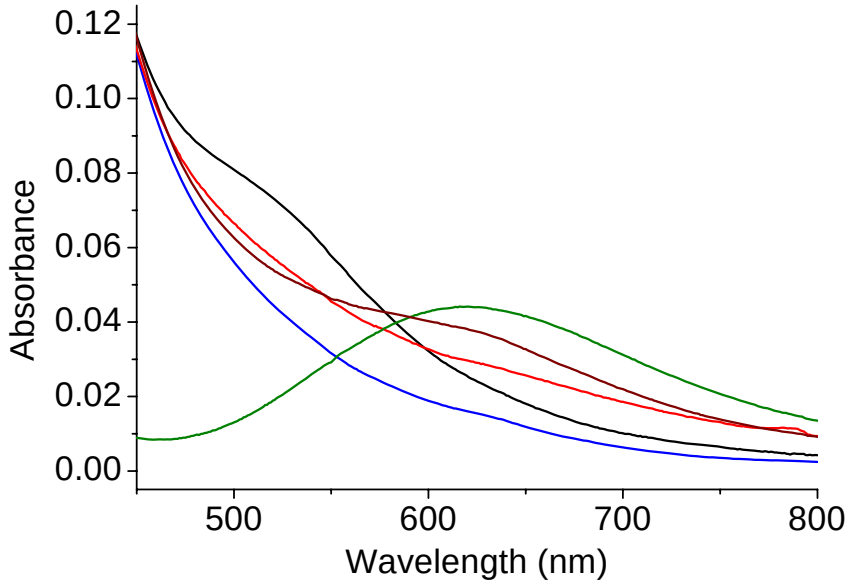

Figure S6. Visible absorption spectra for the interaction of HSA with **5**. Blue: HSA 0.50 mM; black: HSA + $CuCl_2$ (1.7:1, C_{HSA} = 0.50 mM); green: **5** (0.29 mM); red: HSA + **5** (1.7:1, C_{HSA} = 0.50 mM); brown: simulated spectrum for a solution containing HSA (0.50 mM) and **5** (0.29 mM) with no interaction.

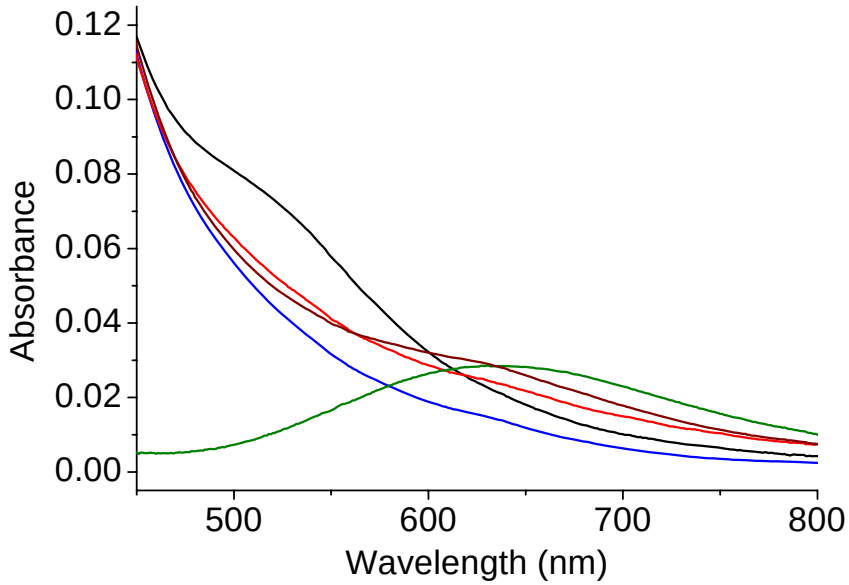

Figure S7. Visible absorption spectra for the interaction of HSA with **6**. Blue: HSA 0.50 mM; black: HSA + $CuCl_2$ (1.7:1, C_{HSA} = 0.50 mM); green: **6** (0.32 mM); red: HSA + **6** (1.6:1, C_{HSA} = 0.50 mM); brown: simulated spectrum for a solution containing HSA (0.50 mM) and **6** (0.32 mM) with no interaction.

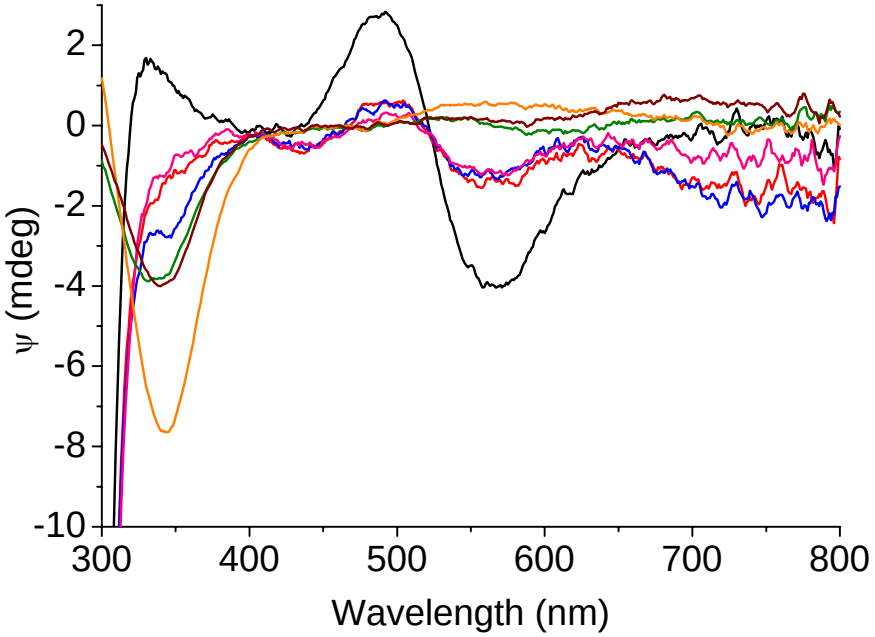

Figure S8. Circular dichroism spectra for the interaction of HSA with compounds **4**-**6**. Black: HSA + $CuCl_2$ (1.7:1, C_{HSA} = 0.50 mM); green: **4** (0.32 mM); orange: **5** (0.29 mM); brown: **6** (0.32 mM); red: HSA + **4** (1.6:1, C_{HSA} = 0.50 mM); blue; HSA + **5** (1.7:1, C_{HSA} = 0.50 mM); magenta HSA + **6** (1.6:1, C_{HSA} = 0.50 mM).

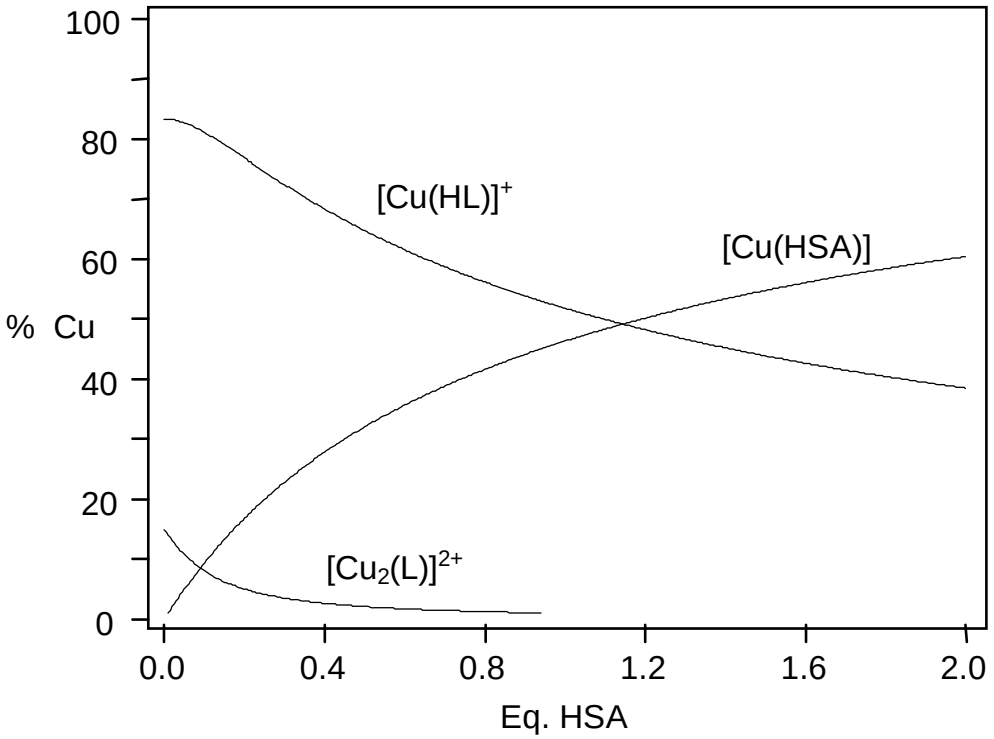

Figure S9. Representative distribution diagram for the addition of HSA to a 0.32 mM solution of **4** at pH 7.4. The speciation model reported in Table 1 and a conditional stability constant of 11.4 for the binding of Cu^{2+} for HSA were used.