Electronic Supplementary Information for Dalton Transactions

Supplementary Information

For the paper

Copper(II) 12-metallacrown-4 of α-, β- and γ-aminohydroxamic acids: a comparative thermodynamic study in aqueous solution

M. Tegoni, M. Remelli, D. Bacco, L. Marchiò, F. Dallavalle

Figure S1. Distribution diagram of the system Cu^{II} / Asp-β-ha (H_2L) (Cu/L = 1:3, $C_{Cu} = 2 \times 10^{-3}$ mol dm^{-3}).

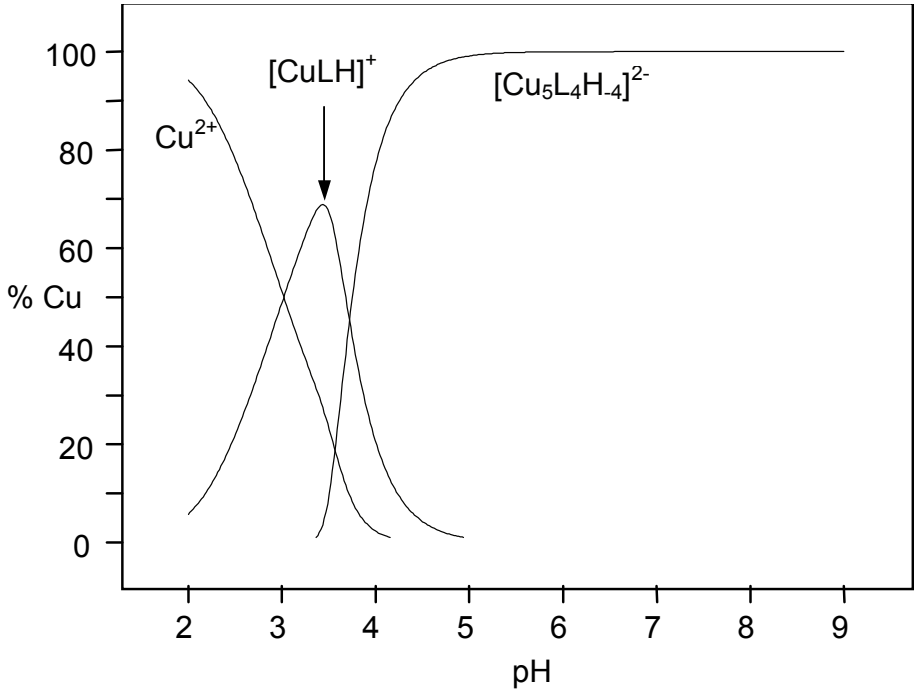


Figure S2. Distribution diagram of the system Cu^{II} / β-Alaha (HL) (Cu/L = 1:3, $C_{Cu} = 2 \times 10^{-3}$ mol dm^{-3}).

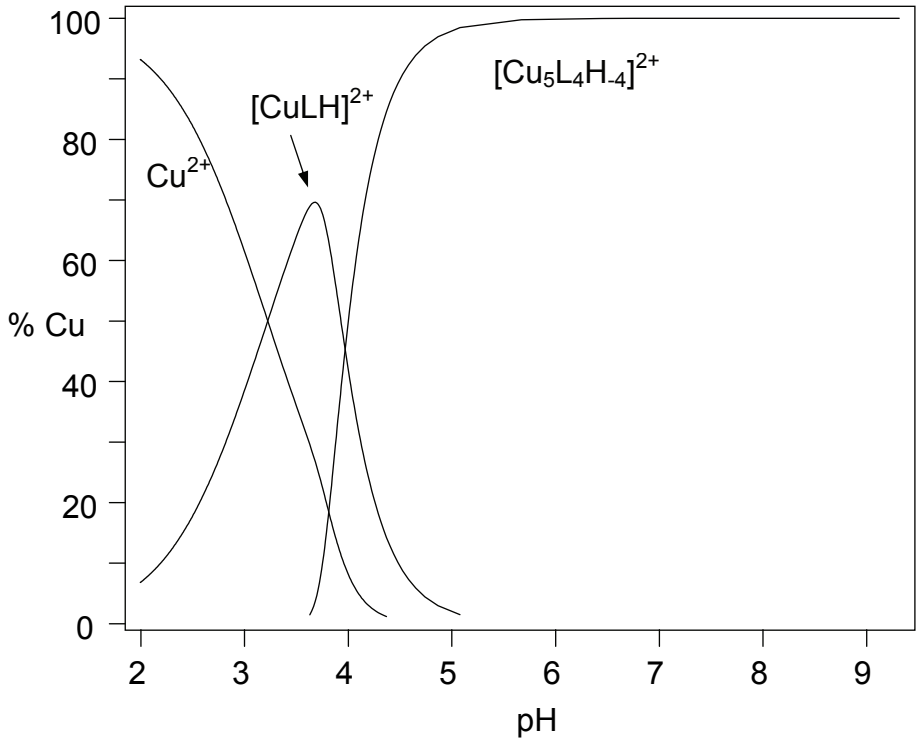


Figure S3. Distribution diagram of the system Cu^{II} / Glu-γ-ha (H_2L) (Cu/L = 1:4, $C_{Cu} = 9 \times 10^{-4}$ mol dm^{-3}).

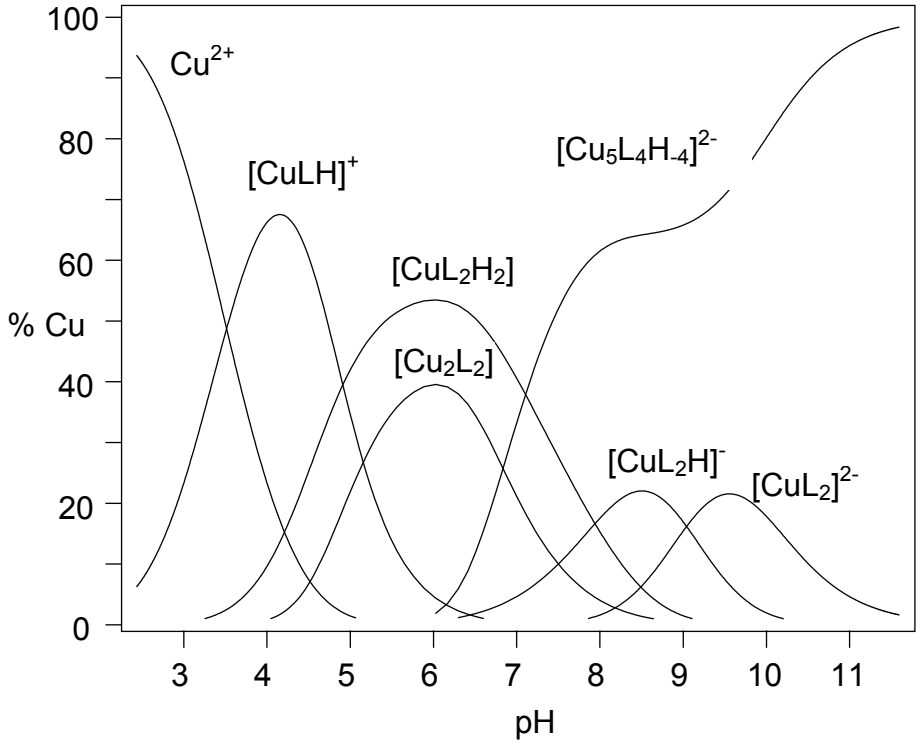
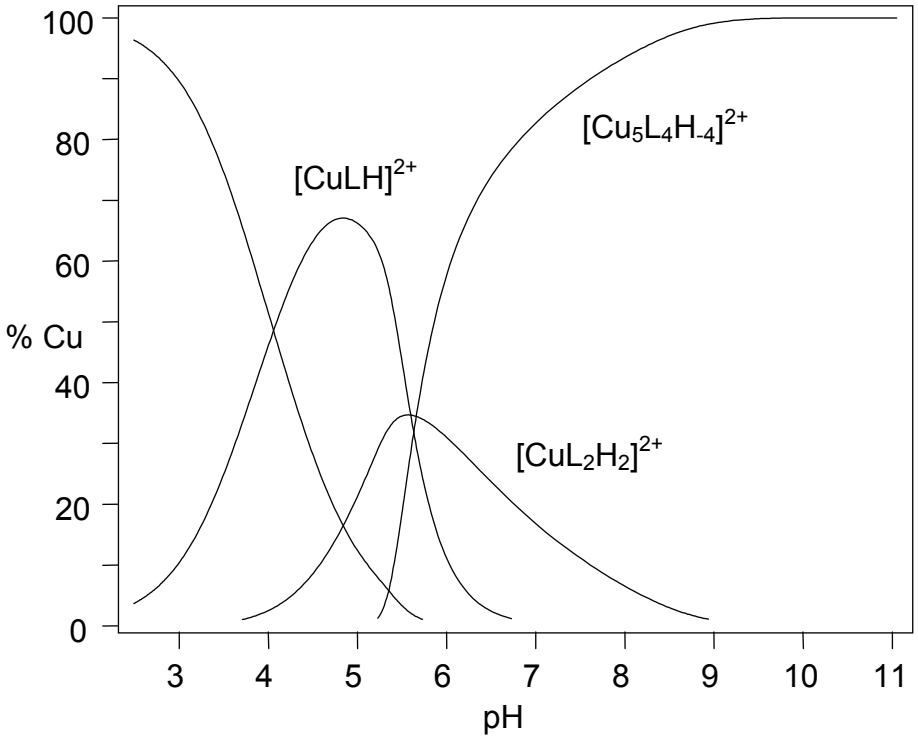
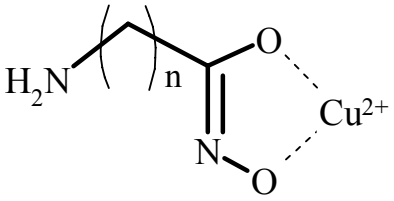


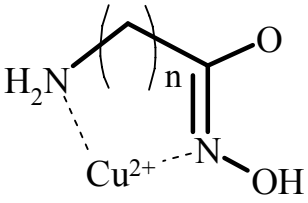
Figure S4. Distribution diagram of the system Cu^{II} / GABAha (HL) (Cu/L = 1:2, $C_{Cu} = 3 \times 10^{-3}$ mol dm^{-3}).



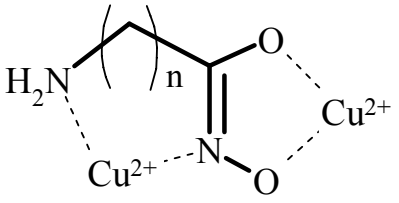
Scheme S1. Schemes of the possible coordination modes for α-, β- and γ- aminohydroxamic acids (n = 1, 2 and 3, respectively). **1**: (*O*,*O*⁻) bidentate; **2**: (*NH*$_2$,*N*⁻) bidentate; **3**: (*NH*$_2$,*N*⁻)-(*O*,*O*⁻) bridging bis-chelating.



1

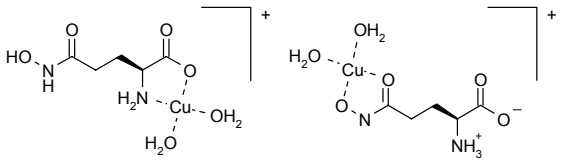


2

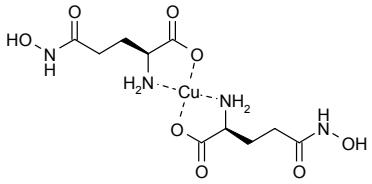


3

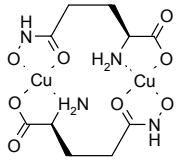
Scheme S2. Schematic structures proposed for the Cu^{II} complexes of Glu-γ-ha.



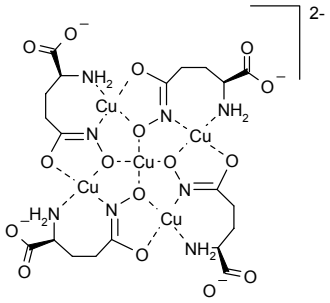
$[CuLH]^{+}$



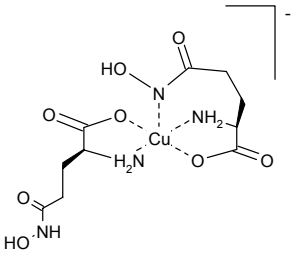
$[CuL_2H_2]$



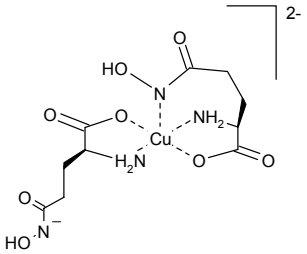
$[Cu_2L_2]$



$[Cu_5L_4H_{-4}]^{2-}$



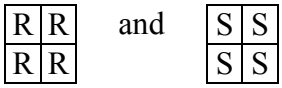
$[CuL_2H]^{-}$



$[CuL_2]^{2-}$

Calculations of the statistical distribution of (*R*)- and (*S*)- ligands in 12-metallacrown-4 by a binomial distribution.

By labelling (*S*)-Valha with S and (*R*)-Valha with R, we can construct the 4-*iso*, 3-*iso*, 1,2-*iso* and 1,3-*iso* isomers as follows:

4-*iso*:  and

3-*iso*:  and 

1,2-*iso*: 

1,3-*iso*: 

Obviously, these calculations are irrespective of the axial or equatorial arrangments of the ligands.

The binomial distribution allows to calculate the probability P of having a certain distribution of R and S over 4 positions (n=4) (P = 1 stands for 100%). The number of S ligands in a certain configuration is ν. Any single position can be occupied by either an S or an R ligand, so that the probability of having an S ligand in a single position is p = ½. The probability of the configurations can be calculated as:

$$P_{(\nu\ \text{S ligands over n=4 positions})} = \frac{n!}{\nu!(n-\nu)!}p^{\nu}(1-p)^{n-\nu} = \frac{3}{2[\nu!(4-\nu)!]}$$

4-*iso*:

The 4-iso can be obtained with both four S ligands (ν = 4) and zero S ligands (ν = 0).
Thus, the probability of having a 4-iso isomer is

$P_{4\text{-}iso} = P_{(4)} + P_{(0)} = 0.125$ (12.5 %)

3-*iso*:

The 3-iso can be obtained with both three S ligands (ν = 3) and one S ligands (ν = 1).
Thus, the probability of having a 3-iso isomer is

$P_{3\text{-}iso} = P_{(3)} + P_{(1)} = 0.5$ (50 %)

1,2-*iso* + 1,3-*iso*

Both these isomers correspond to two S ligands (ν = 2), so the total probability of having one of these two isomers is:

$P_{1,2\text{-}iso+1,3\text{-}iso} = P_{(2)} = 0.375$ (37.5 %)

The probability of having either a 1,2-*iso* or a 1,3-*iso* can be calculated by considering that:

	S			S	S		
R	R	+ S =		R	R		1,2-*iso*
	R			S	R		
S	R	+ S =		S	R		1,2-*iso*
	R			S	R		
R	S	+ S =		R	S		1,3-*iso*

The probability of having one of the three configurations of the first column is the probability of having one S ligand (ν = 1) over three positions, divided by three (all three configurations have the same probability):

$(P_{(\text{one S ligand over n=3 positions})}) / 3 = 1/8 = 0.125$

And thus the probability of having one of the configurations on the second column is the probability of the corresponding on the first column, multiplied by the probability of allocating in the free position an S ligand (p = ½).
The probability of each configuration on the second column is thus 0.125 / 2 = 0.0625.

In a similar way, we can obtain a 1,2-*iso* or 1,3-*iso* isomer also by considering the complementary configurations:

	R			R	R		
S	S	+ R =		S	S		1,2-*iso*
	S			R	S		
R	S	+ R =		R	S		1,2-*iso*
	S			R	S		
S	R	+ R =		S	R		1,3-*iso*

The probability of having one of the three configurations of the first column is the probability of having two S ligand (ν = 2) over three positions, divided by three. Again, each configuration on the second column has a probability of 0.0625.

Thus, the 1,2-*iso* and 1,3-*iso* isomers can be obtained by 4 and 2 different configurations, respectively, on a 0.0625 probability level each:

$P_{1,2\text{-}iso} = 0.0625 \times 4 = 0.25$ (25 %)

$P_{1,3\text{-}iso} = 0.0625 \times 2 = 0.125$ (12.5 %)

As a check, the sum $P_{4\text{-}iso} + P_{3\text{-}iso} + P_{1,2\text{-}iso} + P_{1,3\text{-}iso} = 1$