

## Electronic supplementary information

**Fig. S1** The titration curves of the ligand **L2** and the copper(II)- and zinc(II)-**L2** systems normalised to the total amount of the ligand ( $I = 0.1 \text{ mol dm}^{-3} \text{ NaClO}_4$ ,  $T = 298 \text{ K}$ ).

**Fig. S2** The speciation diagrams of the investigated ligands. The solid lines stand for **L2**, the dashed ones for the **L1** species.  $c_L = 1.0 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $T = 298 \text{ K}$ ,  $I = 0.1 \text{ mol dm}^{-3} \text{ NaClO}_4$ . The charges are denoted to draw attention to the difference between the two ligands.

**Fig. S3** The speciation diagrams of the copper(II)-**L1** systems. (a)  $1.1 \times c_{\text{Cu}^{2+}} = c_{\text{L1}} = 1.0 \times 10^{-3} \text{ mol dm}^{-3}$ ; (b)  $2 \times c_{\text{Cu}^{2+}} = c_{\text{L1}} = 1.0 \times 10^{-3} \text{ mol dm}^{-3}$ ;  $I = 0.1 \text{ mol dm}^{-3} \text{ NaClO}_4$ ;  $T = 298 \text{ K}$ .

**Fig. S4** The speciation diagram of the copper(II)-**L2** system under the conditions of the SOD like activity assay.  $c_{\text{Cu}^{2+}} = 0.9 \times c_{\text{L2}} = 1.0 \times 10^{-6} \text{ mol dm}^{-3}$ ,  $T = 298 \text{ K}$ ,  $I = 0.1 \text{ mol dm}^{-3} \text{ NaClO}_4$ . The dashed lines indicate the pH values of the measurements.

**Fig. S5** The cross peaks related to the secondary amide region in the 2D TOCSY spectra of **L2** in the absence (red) and presence of zinc(II) ions (black). The sample preparation and measurement conditions are described in the Experimental section of the Electronic Supplementary Information. As the figure shows, all the cross peaks of the amide protons found in the ligand spectrum are also detectable in the presence of the metal ion, indicating that no amide deprotonation occurred in the  $\text{ZnH}_2(\text{L2})$  complex.

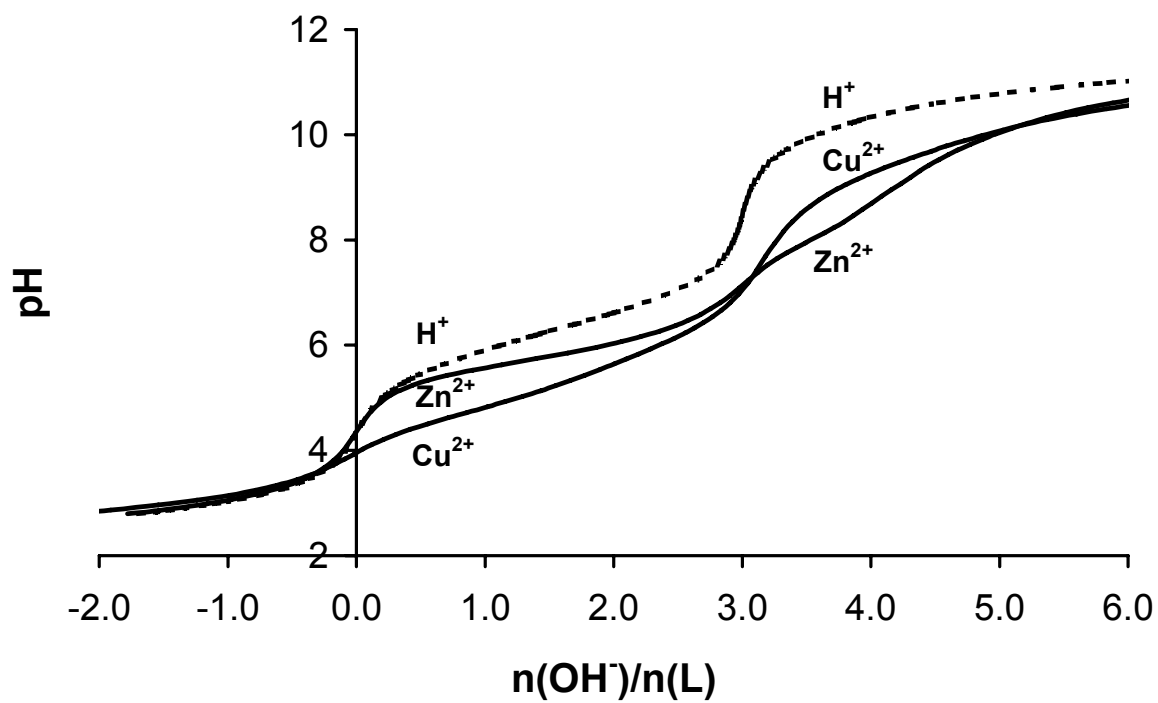


Fig. S1

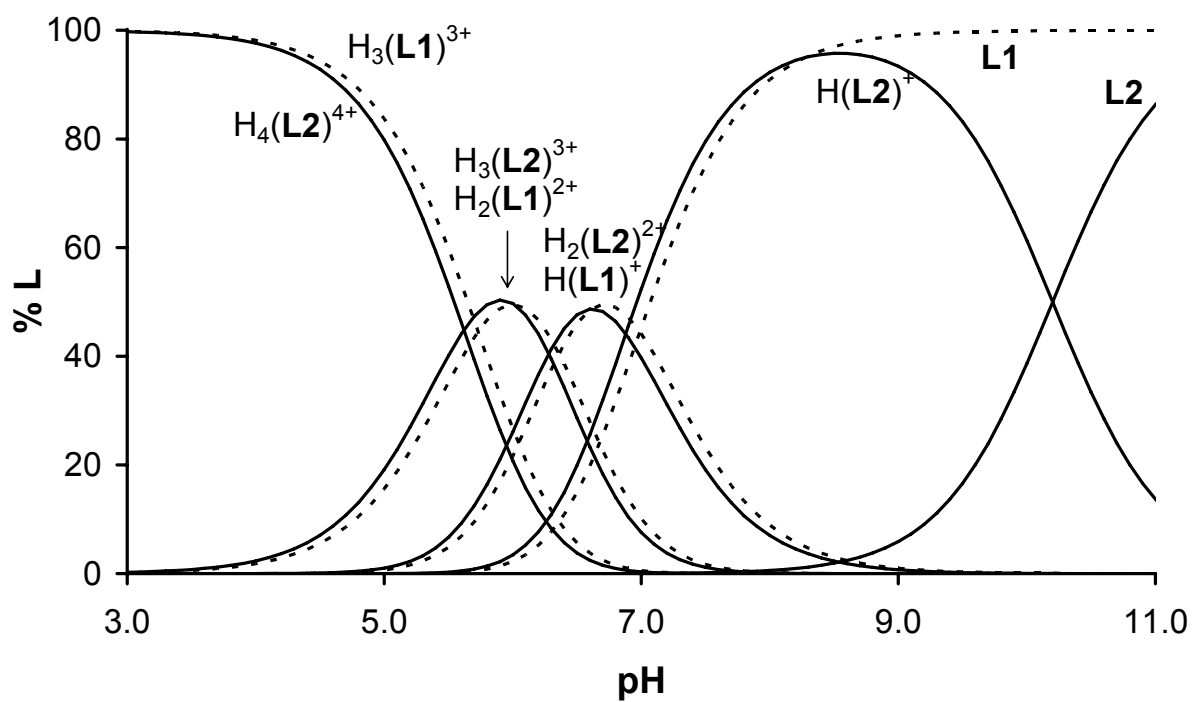
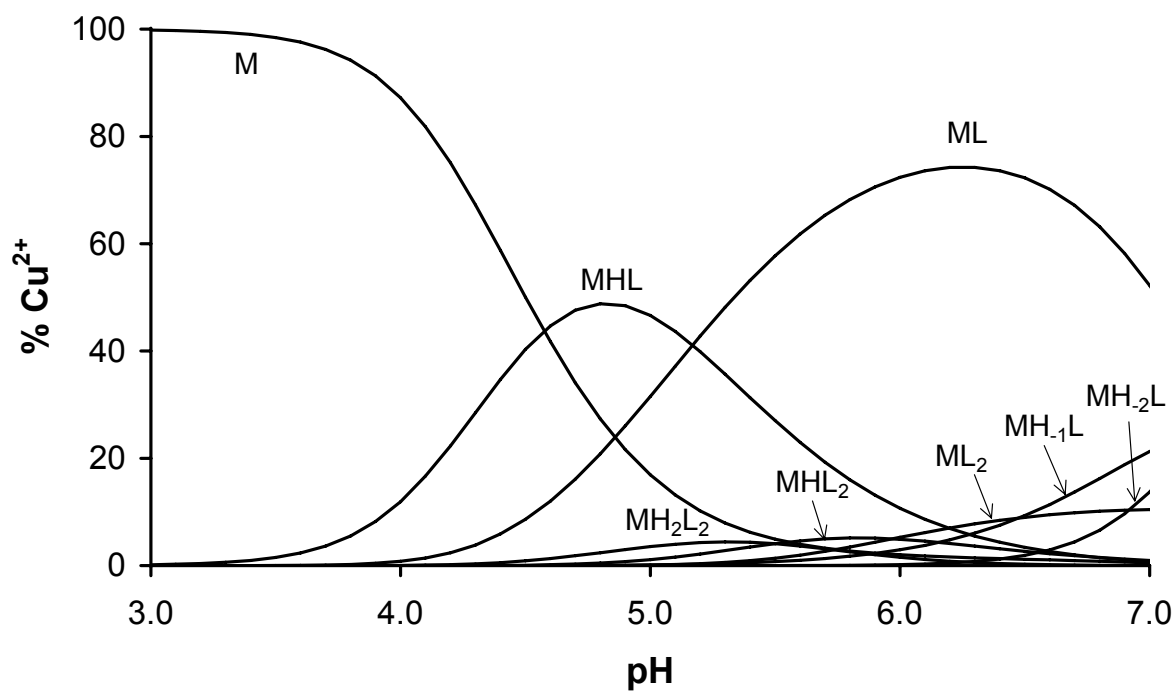


Fig. S2

(a)



(b)

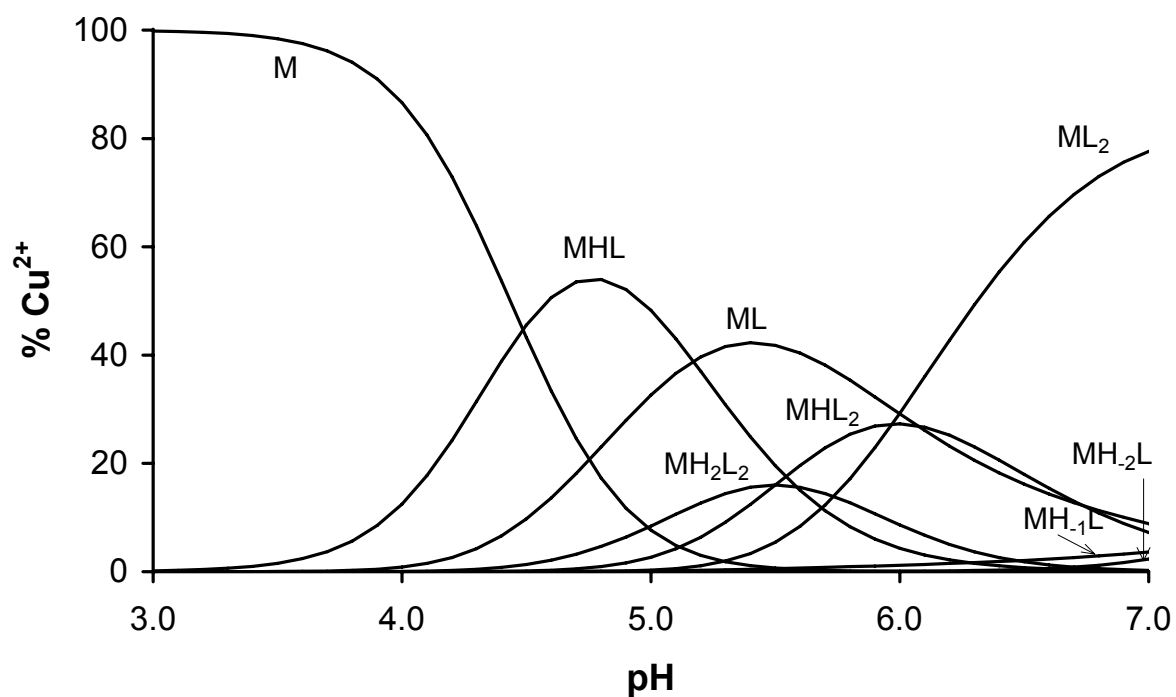


Fig. S3

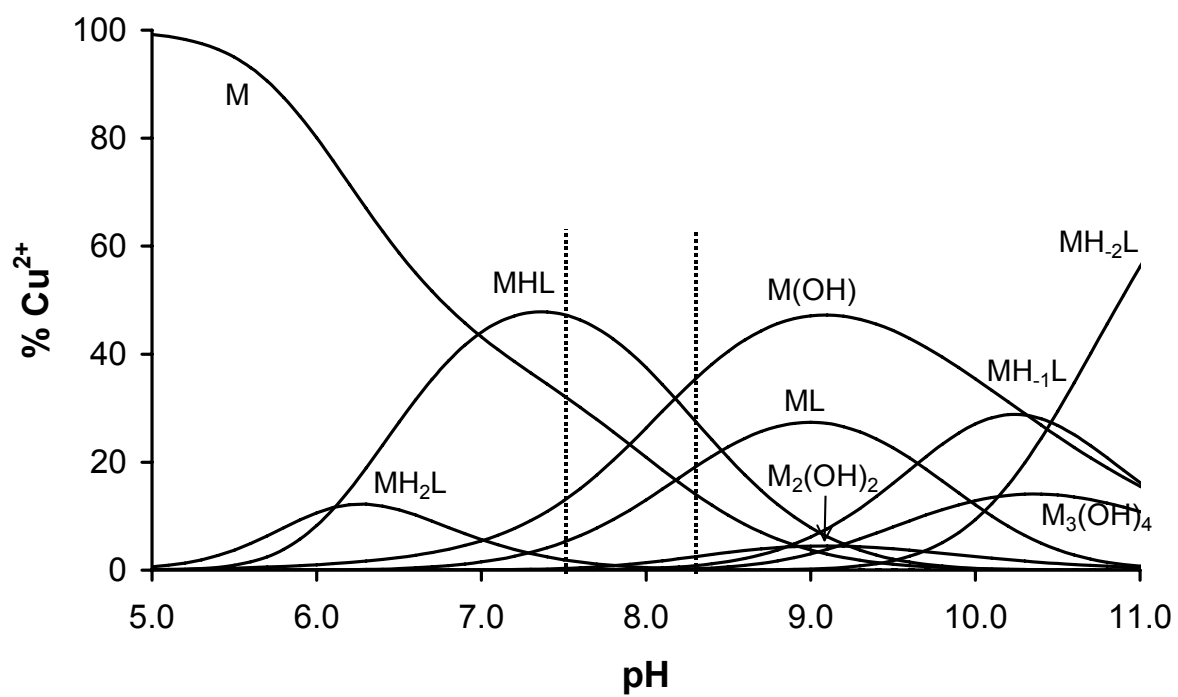


Fig. S4

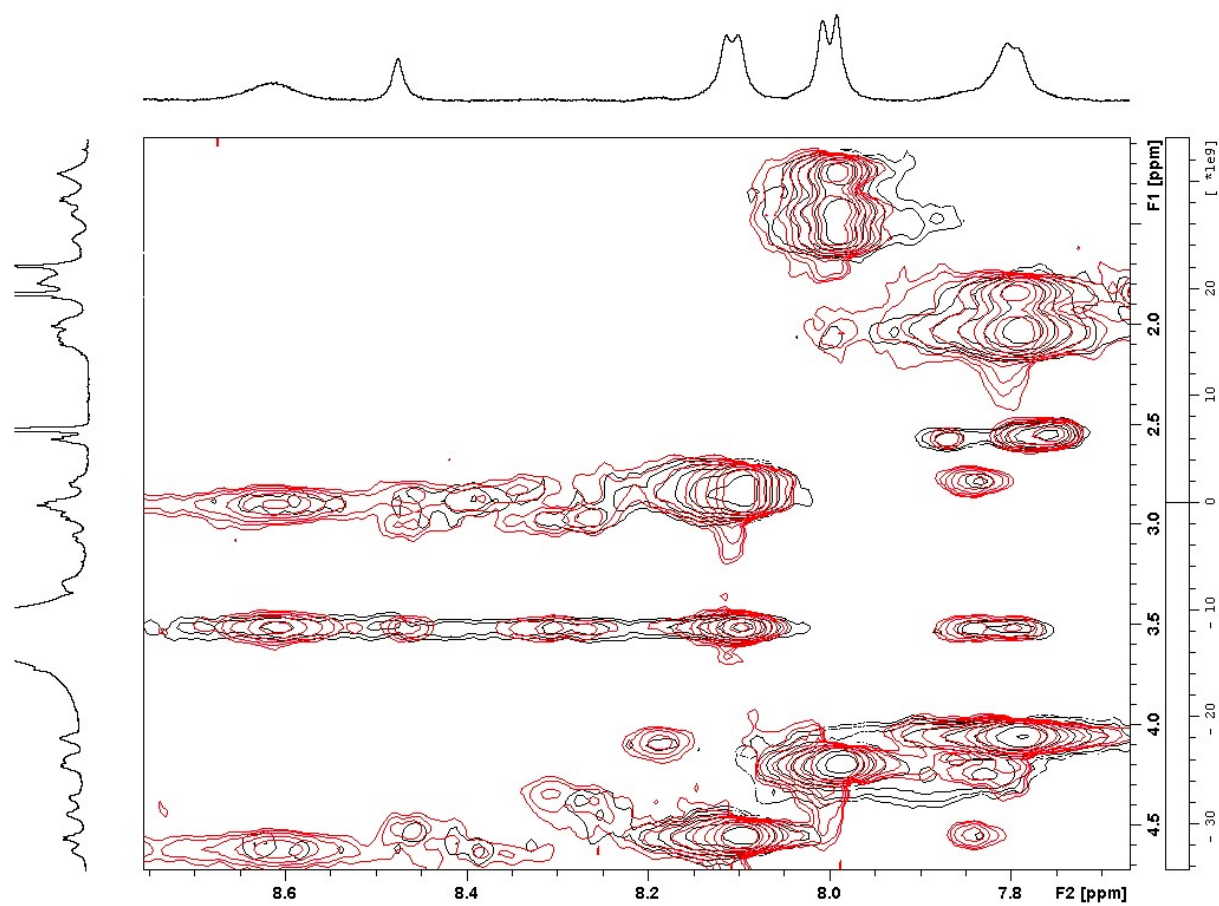


Fig. S5

## Experimental

### NMR measurements

<sup>1</sup>H NMR and 2D TOCSY measurements were performed on a Bruker Ultrashield 600 Plus spectrometer. The spectra were recorded at 25 °C in 100% DMSO-d<sub>6</sub> solution, at a peptide concentration of 3.5 mM (the tube diameter was 5 mm). Two samples of the peptide (with and without zinc(II) ions) were prepared in aqueous solutions by adjusting the pH values to ~ 11.0 where, in the presence of zinc(II), the species ZnH<sub>2</sub>(L2) reaches its formation maximum. The two samples were fast-frozen and lyophilized to dryness and then dissolved in DMSO-d<sub>6</sub>. 2D TOCSY spectra were acquired with 2048(F2)×256(F1) complex points. The experiments employed the MLEV17 sequence with a mixing time of 75 ms. Data were processed using the Topspin 2.0 software package (Bruker).