Supporting Material

Imidazolate Bridged Cu(II)-Cu(II) and Cu(II)-Zn(II) Complexes of a Terpyridinophane Azamacrocycle. A Solution and Solid State Study

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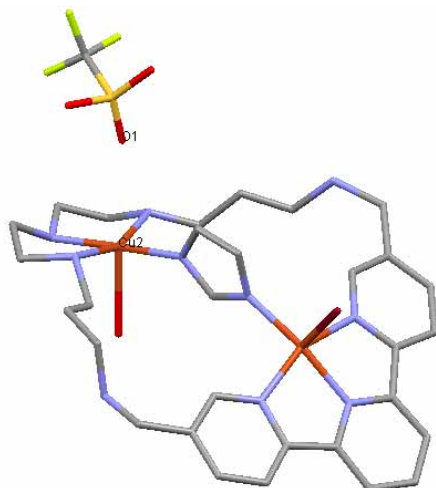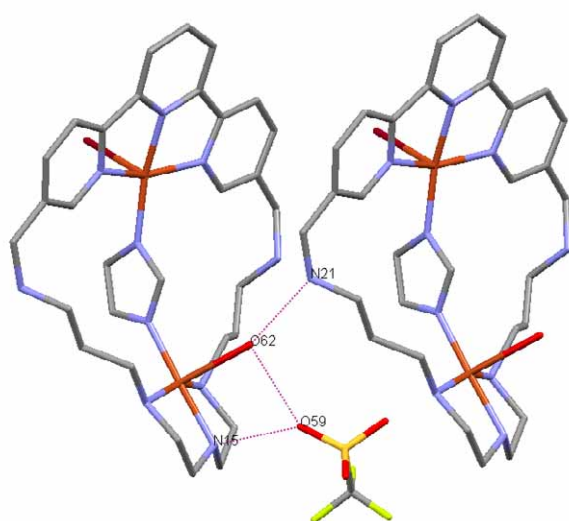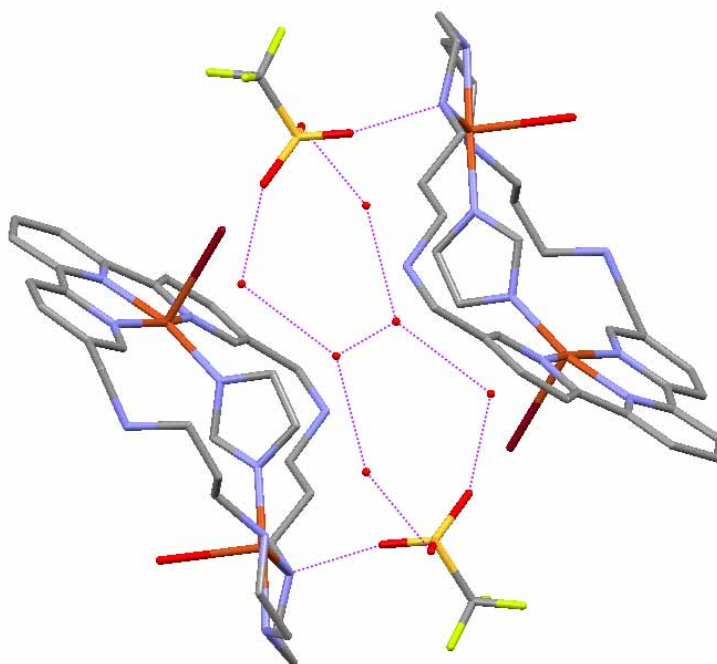
Fig S1.-Draw of the Coordination Site Showing the Long-Range Interaction Cu(2)-O(1)

Fig S2. Repetitive motif detail interconnecting diferent subunits that conform the chain.

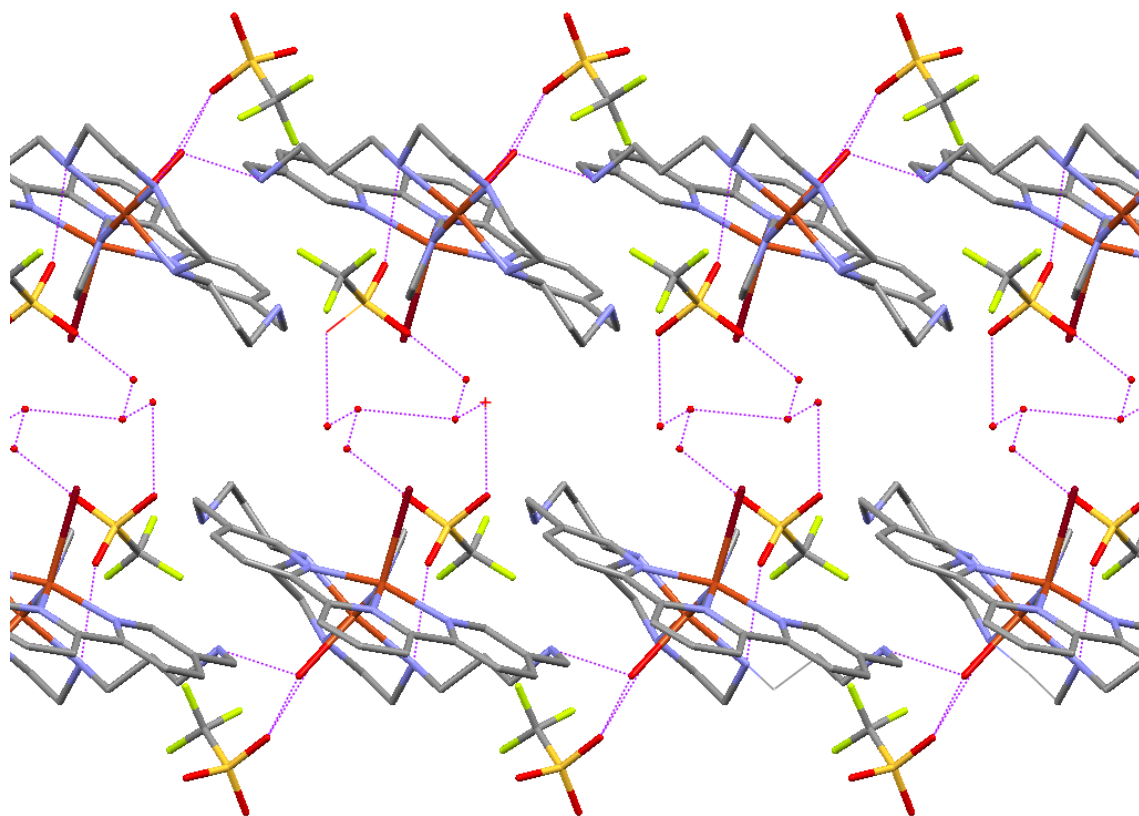**Fig S3**. Repetitive motif that connect opposite chain subunits.

Fig S4. Crystal packing detail along c axis.

Emf Measurements. The potentiometric titrations were carried out at 298.1±0.1 K using $NaClO_4$ 0.15 M as supporting electrolyte. The experimental procedure (burette, potentiometer, cell, stirrer, microcomputer, etc.) has been fully described elsewhere.[1] The acquisition of the emf data was performed with the computer program PASAT.[2] The reference electrode was an Ag/AgCl electrode in saturated KCl solution. The glass electrode was calibrated as a hydrogen-ion concentration probe by titration of previously standardized amounts of HCl with CO_2-free NaOH solutions and the equivalent point determined by the Gran´s method,[3] which gives the standard potential, Eº', and the ionic product of water (pK_W=13.73(1)).

The computer program HYPERQUAD was used to calculate the protonation and stability constants.[4] The pH range investigated was 2.5-11.0 and the concentration of the metal ions and of the ligands ranged from $1x10^{-3}$ to $5x10^{-3}$ M with M:L molar ratios varying from 2:1 to 1:2. For the ternary systems, aqueous solutions at acidic pH containing M:L in 2:1 molar ratios and different amounts of imidazole were titrated with NaOH solutions. In the treatment of the ternary systems the protonation constants of **L** and the stability constants for the formation of Cu^{2+}-**L** and Zn^{2+}-**L** complexes were taken from ref. 5 and those for Cu^{2+}-HIm and Zn^{2+}-HIm from the literature.[6] Introducing these constants as fixed parameters, the constants for the ternary Cu^{2+}-**L**-HIm or Zn^{2+}-**L**-HIm were then calculated. Furthermore, in order to check the consistency of the model, we have then fitted conjointly the titrations of the binary systems Cu^{2+}-**L** or Zn^{2+}-**L** and those of the ternary systems Cu^{2+}-**L**-HIm or Zn^{2+}-**L**-HIm, leaving as parameters to be refined all the constants for the Cu^{2+}-**L** or Zn^{2+}-**L** binary complexes and for the Cu^{2+}-**L**-HIm or Zn^{2+}-**L**-HIm mixed complexes. The model systems obtained were the same in both fittings and the differences between the values of the constants obtained fell within the limits of the standard deviations.

For the quaternary Cu^{2+}-Zn^{2+}-**L**-HIm system, solutions containing Cu^{2+}, Zn^{2+} and **L** in equimolar amounts and different amounts of imidazole were titrated with NaOH. In this case, apart from the constants of the binary Cu^{2+}-**L**, Zn^{2+}-**L**, Cu^{2+}-HIm and Zn^{2+}-HIm, the values of the constants previously determined for the ternary systems Cu^{2+}-Zn^{2+}-**L**, Cu^{2+}-**L**-HIm and Zn^{2+}-**L**-HIm were introduced as fixed parameters in the fitting and the constants for the quaternary systems refined. Similarly to the procedure used for the ternary system, in a next step all titrations corresponding to the ternary and quaternary systems were fitted simultaneously leaving as parameters to be refined all the constants of the ternary and quaternary systems. Again, in this case both procedures gave reproducible chemical models and values of the constants. However, when more than one model could fit the experimental data, the most reliable chemical model was chosen by performing F tests at the 0.05 confidence level.[7,8]

SOD Activity. SOD-like activity was determined by using the nitro blue tetrazolium (NBT) reduction method by the superoxide radical.[9,10] The assay was carried out in an HEPES buffer 50 mM at pH = 7.8 and at room temperature. The kinetics of the NBT reduction to monoformazan (MF) was recorded by reading the absorbance change at 560 nm with the time. Several concentrations of every compound were prepared in TRIS buffer at pH = 7.8. A reaction mixture *ca.* 50 µM in NBT and 175 µM in xanthine in HEPES buffer was prepared. 800 µL of the reaction mixture plus 100 µL of the compound in TRIS buffer were added to 1 mL cuvette. The reaction starts when 100 µL of a solution of xanthine oxidase was added. The xanthine oxidase concentration was optimized to find the appropriate amount that causes the linear absorbance variance during the reading time (2 min). The nonlinear initial induction period is rejected if it exists. The inhibition of the NBT reduction was computed [11] as $(S_0-S)/S_0$, where S_0 and S are the slopes (dA/dt) of the blank (uninhibited) and of the compound, respectively. The IC_{50} values were either read or interpolated from the inhibition vs. concentration plots.[12]

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