

Figure caption

- Figure 1.1 Fig. 1.1 Structure of $[\text{Cu}_2(\text{CH}_3\text{COO})_4(2\text{H}_2\text{O})]$.
- Figure 2.1 ^1H (a) and ^{13}C NMR (b) spectra of H_2L^1 .
- Figure 2.2 ^1H (a) and ^{13}C NMR (b) spectra of H_2L^2 .
- Figure 2.3 Structure of complex **1** with a partial atom-numbering scheme (Hydrogen atoms are omitted for clarity).
- Figure 2.4 Simplified representation of the coordination environment of the four metal centres in complexes **1** and **2**.
- Figure 2.5 2D supramolecular structure of complex **1** formed with C-H... π interactions.
- Figure 2.6 2D supramolecular structure of complex **2** formed with C-H... π and π ... π interactions.
- Figure 2.7 Structure of complex **3** with a partial atom-numbering scheme (Hydrogen atoms are omitted for clarity).
- Figure 2.8 Simplified representation of the coordination environment of the four metal centres in complex **3**.
- Figure 2.9 Arrangement of four copper atoms of complex **3** in a distorted tetrahedron.
- Figure 2.10 Electronic absorption spectra of complexes **1**, **2** and **3**.
- Figure 2.11 Thermal dependence of the χ_{MT} for complexes **1** and **2**. The solid line is a simulation considering the magnetic model shown in Fig.12B for the Type B face-sharing dicubane structure characteristic of complexes **1** and **2**, using the parameters mentioned in the text. The presence of impurities was not considered in the simulation.
- Figure 2.12 A) Structural arrangement of a type B vertex-defective face-sharing dicubane structure like the one of complexes **1** and **2**, where short (equatorial) and long (axial) Cu-O bonds have been illustrated with thick and thin lines, respectively. B) Magnetic model used for the description of structures like those represented in A. C) Structural arrangement of a [4+2] double-open cubane structure like complex **3**, where short (equatorial) and long (axial) Cu-O bonds have been illustrated with thick and thin lines, respectively. D) Magnetic model used for the description of structures like those represented in C.

- Figure 2.13 Thermal dependence of the χ_M and $\chi_M T$ for complex **1**. The solid lines represent the simulation performed considering the magnetic model shown in Fig.12B for the Type B face-sharing dicubane structure characteristic of complexes **1** and **2**, using the parameters mentioned in the text. The presence of 15% impurities with an $S \neq 0$ ground state was considered in the simulation.
- Figure 2.14 Thermal dependence of the $\chi_M T$ for complex **3**. The solid line represents the simulation performed considering the magnetic model shown in Fig. 12D for the [4+2] double-open cubane structure characteristic of complex **3**, using the parameters mentioned in the text.
- Figure 3.1 ^1H NMR spectra of H_2L .
- Figure 3.2 ^{13}C NMR spectra of H_2L .
- Figure 3.3 Molecular structure of **1** (lattice DMF, H_2O molecules and hydrogen atoms are omitted). Only one out of the two orientations of the disordered perchlorate anion and one out of two disordered $-\text{CH}_2-\text{CH}_3$ side chains of three Schiff base are shown for clarity.
- Figure 3.4 Molecular structure of **2**. The hydrogen atoms are omitted for clarity.
- Figure 3.5 Simplified representation of the tetranuclear copper(II) core in **1**.
- Figure 3.6 Simplified representation of the tetranuclearcopper(II) core in **2**.
- Figure 3.7 Arrangement of four copper atoms in complex **1**.
- Figure 3.8 Arrangement of four copper atoms in complex **2**.
- Figure 3.9 2D supramolecular structure of **1** formed by hydrogen bonding and C-H... π interactions.
- Figure 3.10 Simplified representation of C-H... π interactions in complex **2**.
- Figure 3.11 1D supramolecular structure of **2**, formed by hydrogen bonding interactions with lattice terephthalate anion.
- Figure 3.12 IR spectrum of complex **1**.
- Figure 3.13 IR spectrum of complex **2**.
- Figure 3.14 Electronic absorption spectra of complexes**1** and **2**.
- Figure 3.15 Fluorescence spectra of complexes**1-2** (λ_{ex} ,= 370 nm, excitation and emission slit width = 5 nm).

- Figure 3.16 ESI-mass spectrum of **1**.
- Figure 3.17 ESI-mass spectrum of **2**.
- Figure 3.18 UV-Vis absorption spectra BSA (left) and HSA (right) in the presence of increasing amounts (20 μ L 0.755 μ M) of complex **1**.
- Figure 3.19 UV-Vis absorption spectra BSA (left) and HSA (right) in the presence of increasing amounts (20 μ L 0.755 μ M) of complex **2**.
- Figure 3.20 Plot of $1/[\text{complex}]$ vs $1/(A_{\text{obs}}-A_0)$ for interaction of complexes **1-2** with serum albumins.
- Figure 3.21 Fluorescence spectra of BSA ($\lambda_{\text{ex}} = 280$ nm; $\lambda_{\text{em}} = 340$ nm) and HSA ($\lambda_{\text{ex}} = 280$ nm; $\lambda_{\text{em}} = 330$ nm) in the presence of increasing amounts of complex **1** [(A) for BSA, (B) for HSA] and complex **2** [(C) for BSA, (D) for HSA]. Arrows show the emission intensity changes upon increasing complex concentration. Inset: Stern-Volmer plot.
- Figure 3.22 Scatchard plots for complexes **1-2** with BSA / HSA. ($[\text{complex}]$ is the total concentration of added complex).
- Figure 3.23 Absorption spectra of complexes [(A) for **1**; and (B) for **2**] in the absence (black line) and in presence (other lines) of increasing amounts of CT-DNA, at room temperature. Inset: show the plots of $[\text{DNA}]/(\epsilon_a-\epsilon_f)$ vs. $[\text{DNA}]$. The arrows show the absorbance change with increasing CT-DNA concentration.
- Figure 3.24 Effect of addition of complexes **1** (A) and **2** (B) on the emission intensity of EB bounded CT-DNA. Inset: Stern-Volmer plots of fluorescence titrations.
- Figure 3.25 Cyclic voltammograms of **1** (black) and **2** (red).
- Figure 4.1 Molecular structure of **1** with labeling of selected atoms. The structure displays some disorder, some atoms were refined over two positions, and other ones were refined using constraints.
- Figure 4.2 Molecular structure **2** with labeling of selected atoms.
- Figure 4.3 Representation of the tetranuclear copper(II) core in **1** with the coordination environment of the copper(II) centers.
- Figure 4.4 Representation of the tetranuclear copper(II) core in **2** with the coordination environment of the copper(II) centers.

- Figure 4.5 Arrangement of four copper atoms in complex **1**.
- Figure 4.6 Arrangement of four copper atoms in complex **2**.
- Figure 4.7 1D supramolecular architecture of **1** formed by C-H... π interactions.
- Figure 4.8 1D supramolecular architecture of **2** formed by C-H... π interactions.
- Figure 4.9 IR spectrum of complex **1**.
- Figure 4.10 IR spectrum of complex **2**.
- Figure 4.11 Absorption spectra of complex **1** (black line) and complex **2** (red line).
- Figure 4.12 Fluorescence spectra of complex **1** (black line) and complex **2** (red line). ($\lambda_{\text{ex}} = 267$ nm for **1** and $\lambda_{\text{ex}} = 277$ nm for **2**. Excitation and emission slit width = 5 nm).
- Figure 4.13 UV-Vis absorption spectra of **1**-BSA (left) and **2**-BSA (right) upon gradual addition of 10 μl 0.3475 μM aqueous solutions of complexes at room temperature.
- Figure 4.14 UV-Vis absorption spectra of **1**-HSA (left) and **2**-HSA (right) upon gradual addition of 10 μl 0.3475 μM aqueous solutions of complexes at room temperature.
- Figure 4.15 Plot of $1/[\text{complex}]$ vs $1/(A_{\text{obs}}-A_0)$ for the calculation of apparent association constant (K_{app}).
- Figure 4.16 Emission spectrum of BSA ($\lambda_{\text{ex}} = 280$ nm; $\lambda_{\text{em}} = 340$ nm) and HSA in the presence of increasing amounts of complexes. Arrow shows that the emission intensity changes upon increasing complex concentration.
- Figure 4.17 Scatchard plot of the SA fluorescence titration for complexes.
- Figure 4.18 Absorption titration spectra of complexes **1** and **2** in the absence (black line) and presence (other lines) of CT-DNA to complex at room temperature. Inset: Plot of $[\text{DNA}]/(\epsilon_{\text{a}}-\epsilon_{\text{f}})$ versus $[\text{DNA}]$. Arrow shows the absorbance changes upon increasing CT-DNA concentration.
- Figure 4.19 Emission spectra of EB bounded CT-DNA in the presence of complex **1** (A) and complex **2** (B). Inset: Stern-Volmer plot of fluorescence titrations.
- Figure 4.20 Molecular docked model of complexes **1** (a) and **2** (b) with DNA (PDB ID: 1BNA)
- Figure 4.21 Molecular docking image of complex **1** with BSA (binding site: Tyr149); (a)

Interaction of **1** with amino acid residues of BSA (b) Zoom view of interaction of **1** with amino acid residues of BSA (c) H-bonding interaction of **1** with amino acid residues of BSA

Figure 4.22 Molecular docking image of complex **2** with BSA (binding site: Tyr149); (a) Interaction of **2** with amino acid residues of BSA (b) Zoom view of interaction of **2** with amino acid residues of BSA (c) H-bonding interaction of **2** with amino acid residues of BSA.

Figure 4.23 Molecular docking image of complex **1** with BSA (binding site: Tyr410); (a) Interaction of **1** with amino acid residues of BSA (b) Zoom view of interaction of **1** with amino acid residues of BSA (c) H-bonding interaction of **1** with amino acid residues of BSA.

Figure 4.24 Molecular docking image of complex **2** with BSA (binding site: Tyr410); (a) Interaction of **2** with amino acid residues of BSA (b) Zoom view of interaction of **2** with amino acid residues of BSA (c) H-bonding interaction of **2** with amino acid residues of BSA.

Figure 4.25 Molecular docking image of complex **2** with HSA (binding site: Tyr150); (a) Interaction of **2** with amino acid residues of HSA (b) Zoom view of interaction of **2** with amino acid residues of HSA (c) H-bonding interaction of **2** with amino acid residues of HSA.

Figure 4.26 Molecular docking image of complex **1** with HSA (binding site: Tyr150); (a) Interaction of **2** with amino acid residues of HSA (b) Zoom view of interaction of **2** with amino acid residues of HSA.

Figure 4.27 Molecular docking image of complex **1** with HSA (binding site: Tyr407); (a) Interaction of **1** with amino acid residues of HSA (b) Zoom view of interaction of **1** with amino acid residues of HSA (c) H-bonding interaction of **1** with amino acid residues of HSA.

Figure 4.28 Molecular docking image of complex **2** with HSA (binding site: Tyr407); (a) Interaction of **2** with amino acid residues of HSA (b) Zoom view of interaction of **2** with amino acid residues of HSA.

Figure 5.1 ORTEP view of the asymmetric unit of complex **1** showing the thermal ellipsoids at 30% probability level.

- Figure 5.2 The polymeric structure of complex **1** determined by the Cu1...O5 and Cu2...O3 interactions.
- Figure 5.3 2D supramolecular sheet of complex **1** formed with $\pi \dots \pi$ interactions.
- Figure 5.4 3D supramolecular structure of complex **1** formed with $\pi \dots \pi$ and C-H... π interactions.
- Figure 5.5 Asymmetric unit of complex **2**.
- Figure 5.6 The 1D polymeric structure of complex **2**. The lattice water molecule and hydrogen atoms have been omitted for clarity.
- Figure 5.7 2D supramolecular sheet formed by the C-H... π interaction in complex **2**.
- Figure 5.8 2D supramolecular sheet formed by the C-H... π interaction (in space fill mode).
- Figure 5.9 3D supramolecular network formed by the C-H... π interaction.
- Figure 5.10 Electronic absorption and emission spectra of complex **1**.
- Figure 5.11 Electronic absorption and emission spectra of complex **2**.
- Figure 5.12 Change of electronic absorption spectra of BSA (**a**) and HSA (**b**) upon gradual addition of complex **1** at temperature 300 K.
- Figure 5.13 Change of electronic absorption spectra of BSA (**a**) and HSA (**b**) upon gradual addition of complex **2** at temperature 300 K.
- Figure 5.14 Plot of $1/(A_{\text{obs}} - A_0)$ versus reciprocal of complex **1** concentration for titration with BSA (**a**) and HSA (**b**) at 300 K.
- Figure 5.15 Plot of $1/(A_{\text{obs}} - A_0)$ versus reciprocal of complex **2** concentration for titration with BSA and HSA at 300 K.
- Figure 5.16 Fluorescence quenching curves of BSA (**a**) and HSA (**b**) in the presence of increasing amounts of complex **1** (0-11.269 μM). Arrow shows that the emission intensity changes upon increasing complex concentration (Inset: Stern-Volmer plot of the fluorescence titration).
- Figure 5.17 Emission spectrum of BSA (**A**) and HSA (**B**) in the presence of increasing amounts of complexes **2** (0-11.269 μM). Arrow shows that the emission intensity changes upon increasing complex concentration (Inset: Stern-Volmer plot of the fluorescence titration).
- Figure 5.18 Double-logarithm curves of BSA and HSA fluorescence quenching by **1**.

- Figure 5.19 Double-logarithm curves of BSA and HSA fluorescence quenching by complex **2**.
- Figure 5.20 Change of electronic absorption spectra of complex **1** upon gradual addition of aqueous solution of CT-DNA. Inset: Plot of $[\text{DNA}] / (\epsilon_a - \epsilon_f)$ versus $[\text{DNA}]$. Arrows show the changes in absorbance with respect to an increase in the DNA concentration.
- Figure 5.21 Absorption titration spectra of complex **3** in the absence (black line) and presence (other lines) of CT-DNA to complex at room temperature. Inset: Plot of $[\text{DNA}] / (\epsilon_a - \epsilon_f)$ versus $[\text{DNA}]$. Arrow shows the absorbance changes upon increasing CT-DNA concentration.
- Figure 5.22 Fluorescence quenching curves of EB bound to CT-DNA in the presence of complex **1**. Inset: Stern-Volmer plot of fluorescence titration.
- Figure 5.23 Fluorescence quenching curves of EB bound to CT-DNA in the presence of complex **2**. Inset: Stern-Volmer plot of fluorescence titration.
- Figure 5.24 $\chi_M T$ versus T plot for complex **1** (solid line represents the best fit).
- Figure 5.25 Thermal dependence of the $\chi_M T$ for complex **2**. The straight line represents the fit obtained considering a Cu(II) dinuclear model and using the Hamiltonian and parameters mentioned in the text.
- Figure 6.1 Molecular structure of tetranuclear cubane in **1** with labeling of selected atoms. The lattice water molecule and hydrogen atoms have been omitted for clarity.
- Figure 6.2 Representation of the tetranuclear copper(II) core in **1** with the coordination environment of metal centers.
- Figure 6.3 Molecular structure **2** with labeling of selected atoms. The lattice water molecules, lattice squarate anion and hydrogen atoms have been omitted for clarity.
- Figure 6.4 Representation of the tetranuclear copper(II) core in **2** with the coordination environment of the metal centers.
- Figure 6.5 Absorption spectra of complexes **1-2**.
- Figure 6.6 Fluorescence spectra of complexes **1-2**. [$\lambda_{\text{ex}} = 343$ nm (for **1**), 370 nm (for **2**), excitation and emission slit width = 5 nm].

- Figure 6.7 Thermal dependence of the χ_{MT} for complexes **1** and **2**. The solid lines are the fits obtained considering the models of Fig. 6.8 and using the Hamiltonian and parameters mentioned in the text.
- Figure 6.8 A) Structural arrangement of a [4+2] cubane structure as that of complex **1** and C) of a [4+2] double-open cubane structure as that of complex **2**: short (equatorial) and long (axial) Cu-O bonds are illustrated with thick and thin lines, respectively. B, D) Exchange coupling models used for the magnetic analysis of complexes **1** and **2**, respectively.
- Figure 6.9 UV-visible absorption spectra of serum albumins in the absence and presence of the complexes **1-2**.
- Figure 6.10 Change of electronic absorption spectra of BSA (A for **1**; B for **2**) and HSA (C for **1**; D for **2**) upon gradual addition of complexes **1-2** at temperature 300 K.
- Figure 6.11 Emission spectrum of BSA ($\lambda_{ex} = 280$ nm; $\lambda_{em} = 340$ nm) and HSA ($\lambda_{ex} = 280$ nm; $\lambda_{em} = 330$ nm) in the presence of increasing amounts (0 - 11.2 μ M) of complexes **1** (A, C) and **2** (B, D). Arrow shows that the emission intensity changes upon increasing complex concentration. Inset: Stern-Volmer plot.
- Figure 6.12 Scatchard plots of the SAs fluorescence titration for complexes **1-2**.
- Figure 6.13 Absorption titration spectra of complexes **1** (left) and **2** (right) in the absence (black line) and presence (other lines) of CT-DNA to complex at room temperature. Inset: Plot of $[DNA]/(\epsilon_a - \epsilon_f)$ versus $[DNA]$. Arrow shows the absorbance changes upon increasing CT-DNA concentration.
- Figure 6.14 Emission spectra of EB bounded CT-DNA in the presence of complex **1** (A) and **2** (B). Inset: Stern-Volmer plot of fluorescence titrations.
- Figure 6.15 Molecular docked model of complexes **1** (a) and **2** (b) with DNA (PDB ID: 1BNA)
- Figure 6.16 Molecular docking image of complex **1** with BSA (binding site: Tyr149); (a) Interaction of **1** with amino acid residues of BSA (b) H-bonding interaction of **1** with amino acid residues of BSA (c) Surface plot (d) Zoom view of surface plot.

- Figure 6.17 Molecular docking image of complex **1** with BSA (binding site: Tyr410); (a) Interaction of **1** with amino acid residues of BSA (b) Surface plot (c) Zoom view of surface plot.
- Figure 6.18 Molecular docking image of complex **2** with BSA (binding site: Tyr149); (a) Interaction of **2** with amino acid residues of BSA (b) H-bonding interaction of **2** with amino acid residues of BSA (c) Surface plot (d) Zoom view of surface plot.
- Figure 6.19 Molecular docking image of complex **2** with BSA (binding site: Tyr410); (a) Interaction of **2** with amino acid residues of BSA (b) H-bonding interaction of **2** with amino acid residues of BSA (c) Surface plot (d) Zoom view of surface plot.
- Figure 6.20 Molecular docking image of complex **1** with HSA (binding site: Tyr150); (a) Interaction of **1** with amino acid residues of HSA (b) H-bonding interaction of **1** with amino acid residues of HSA (c) Surface plot (d) Zoom view of surface plot.
- Figure 6.21 Molecular docking image of complex **1** with HSA (binding site: Tyr407); (a) Interaction of **1** with amino acid residues of HSA (b) H-bonding interaction of **1** with amino acid residues of HSA (c) Surface plot (d) Zoom view of surface plot.
- Figure 6.22 Molecular docking image of complex **2** with HSA (binding site: Tyr150); (a) Interaction of **2** with amino acid residues of HSA (b) H-bonding interaction of **2** with amino acid residues of HSA (c) Surface plot (d) Zoom view of surface plot.
- Figure 6.23 Molecular docking image of complex **2** with HSA (binding site: Tyr407); (a) Interaction of **2** with amino acid residues of HSA (b) H-bonding interaction of **2** with amino acid residues of HSA (c) Surface plot (d) Zoom view of surface plot.