Figure caption

Figure 1.1. Schematic figure of complex $[Co(bipy)(NO_3)_2(CH_3CN)]$

Figure 1.2. Schematic figure of complex $[Co(phen)(NO_3)_2(CH_3CN)]$

Figure 1.3. Schematic figure of complex $[Co(III)(bipy)_2(N_3)_2]Cl$

Figure 1.4. Schematic figure of complex $[Cu(bipy)_2(NO_3)]ClO_4$

Figure 1.5. Schematic figure of complex $[Cu(phen)_2(H_2O)](ClO_4)_2$

Figure 1.6. Schematic figure of complex $[Cu_2(ox)(phen)_2(H_2O)_2](NO_3)_2$

Figure 1.7. Schematic figure of complex trans-$(H_2ben)[Co(2,5\text{-}pdc)_2(H_2O)_2]\cdot 4H_2O$

Figure 1.8. Schematic figure of complex $\{[Cu(2,5\text{-}pdc)(H_2O)_4]\cdot H_2O\}$

Figure 1.9. Schematic figure of complex $[Cu(\mu_4\text{-}abdc)\ (DMF)]_n$

Figure 1.10. Schematic figure of complex $[Co_2(3,5\text{-}pdc)_2(bpy)_2(H_2O)_4]\cdot 4H_2O$

Figure 1.11. δ bond formation and dimeric structure of copper(II) acetate monohydrate.

Figure 1.12. linear superexchange pathway.

Figure 1.13. 90° superexchange pathway.

Figure 1.14a. Schematic representation of Plastocyanin.

Figure 1.14b. Schematic representation of galactose oxidase.

Figure 1.14c. Schematic representation of Oxyhemocyanine.

Figure 1.15. Schematic figure of seven dinuclear Cu(II) complexes.

Figure 2.1. ^1H NMR (a) and ^{13}C NMR (b) spectra of H_4L.

Figure 2.2. View of molecular models built from the experimental crystal structures of **1** (a) and **2** (b) and used in NEVPT2 calculations to evaluate the *zfs* parameters, *D* and *E*. Cobalt, nitrogen, oxygen, carbon and hydrogen atoms are displayed in magenta, light blue, red, grey and pink colours, respectively.

Figure 2.3. Crystal packing of **1**: the *m*-phth anion, the coordinated aqua ligand O2w, and lattice water molecules O4w–O9w (all at half occupancy) share the same area owing to the crystallographic symmetry center represented by the black dot.

Figure 2.4. ORTEP drawing (40 % probability ellipsoids) of the $[Co_2(H_2L)_2(H_2O)\text{-}(m\text{-phth})]^-$ anion of **1**. The labels of the C atoms are omitted for clarity.

Figure 2.5. ORTEP drawing (50 % probability ellipsoids) of the centrosymmetric molecular structure of **2** (labels of C atoms omitted for clarity).

Figure 2.6. Thermal dependence of $\chi_M T$ of **1** under applied dc fields of 0.25 ($T < 30$ K) and 5.0 kG ($T \geq 30$ K): () experimental data; (–) best-fit curve (see text). The inset shows the dependence of *M* with *H* for **1** at 2.0, 2.5, 3.0, 4.0, 5.0, 7.0, 8.0, 9.0 and 10.0 K (from black to palest grey dots). The solid lines are the best-fit curves (see text).

Figure 2.7. Thermal dependence of $\chi_M T$ of **2** under applied dc fields of 0.25 ($T < 30$ K) and 5.0 kG ($T \geq 30$ K): () experimental data; (–) best-fit curve (see text). The inset shows the dependence of *M* with *H* for **2** at 2.0, 2.5, 3.0, 4.0, 5.0, 7.0, 8.0, 9.0 and 10.0 K (from black to palest grey dots). The solid lines are the best-fit curves (see text).

Figure 2.8. Dependence of *M* with *H*/*T* of **1** in a temperature range starting at 2.0, 2.5, 3.0, 4.0, 5.0, 7.0, 8.0, 9.0 and 10.0 K (from black to palest grey dots).

Figure 2.9. Dependence of *M* with *H*/*T* of **2** in a temperature range starting at 2.0, 2.5, 3.0, 4.0, 5.0, 7.0, 8.0, 9.0 and 10.0 K (from black to palest grey dots).

Figure 2.10. Temperature dependence of (a) χ_M' and (b) χ_M'' (b) of **1** in a dc applied static field of 1.0 kG and under ±4.0 G oscillating field at frequencies in the range 1.0–10 kHz. (c) The Cole–Cole plot at 5.0–7.0 K and (d) the Arrhenius plot in the high-temperature region for an applied static field of 1.0 kG.

Figure 2.11. Temperature dependence of (a) χ_M' and (b) χ_M'' (b) of **2** in a dc applied static field of 1.0 kG and under ±4.0 G oscillating field at frequencies in the range 1.0–10 kHz. (c)

The Cole–Cole plot at 6.0–8.0 K and (d) the Arrhenius plot in the high-temperature region for an applied static field of 1.0 kG.

Figure 2.12. Temperature dependence of χ_M‘ (a) and χ_M“ (b) of **1** in a dc applied static field of 0.5 kG and under ±4.0 G oscillating field at frequencies in the range of 1.0–10 kHz. The Cole-Cole plot (c) at 5.0–7.0 K and the Arrhenius plot in the high temperature region (d) for an applied static field of 0.5 kG.

Figure 2.13. Temperature dependence of χ_M‘ (a) and χ_M“ (b) of **1** in a dc applied static field of 2.5 kG and under ±4.0 G oscillating field at frequencies in the range of 1.0–10 kHz. The Cole-Cole plot (c) at 5.0–7.0 K and the Arrhenius plot in the high temperature region (d) for an applied static field of 2.5 kG.

Figure 2.14. Temperature dependence of χ_M‘ (a) and χ_M“ (b) of **2** in a dc applied static field of 0.5 kG and under ±4.0 G oscillating field at frequencies in the range of 1.0–10 kHz. The Cole-Cole plot (c) at 6.0–8.0 K and the Arrhenius plot in the high temperature region (d) for an applied static field of 0.5 kG.

Figure 2.15. Temperature dependence of χ_M‘ (a) and χ_M“ (b) of **2** in a dc applied static field of 2.5 kG and under ±4.0 G oscillating field at frequencies in the range of 1.0–10 kHz. The Cole-Cole plot (c) at 6.0–8.0 K and the Arrhenius plot in the high temperature region (d) for an applied static field of 2.5 kG.

Figure 2.16. IR spectra of H_4L, **1** and **2**.

Figure 2.17. UV-Vis absorption spectra of H_4L, **1** and **2**.

Figure 2.18. ESI-mass spectra of complex **1** (a) and **2** (b) recorded in methanol.

Figure 2.19. Experimental and simulated X-ray powder diffraction pattern of complex **1**.

Figure 2.20. Experimental and simulated X-ray powder diffraction pattern of complex **2**.

Figure 3.1. ^{1}H and ^{13}C NMR spectrum of H_2L^1 recorded in $CDCl_3$.

Figure 3.2. ^{1}H (a) and ^{13}C (b) NMR spectra of H_4L^2 recorded in d_6-DMSO.

Figure 3.3. Molecular structure of complex **1** (dotted lines indicate long Cu-O bond distances).

Figure 3.4. Molecular structure of complex **2** (dotted lines indicate long Cu-O bond distances). The water molecule bound at each copper ion (Cu-Ow=2.797(6) Å) not shown for sake of clarity.

Figure 3.5. Complex **1** viewed down the S_4 symmetry axis and a perspective side view (H-atoms and ethyl groups not shown).

Figure 3.6. Complex **2** viewed down the S_4 symmetry axis and a perspective side view (H-atoms, methoxy and CH_2OH groups removed for clarity). The ligands arrangement is similar to that detected in all the complexes structurally characterized and reported to date.

Figure 3.7. Electronic spectra of ligand H_2L^1 (blue) and H_4L^2 (black).

Figure 3.8. IR spectrum of complex **1** (blue) and **2** (black).

Figure 3.9. Absorption (left) and fluorescence (right) spectra of complex **1**.

Figure 3.10. Absorption (left) and fluorescence (right) spectra of complex **2**.

Figure 3.11. Thermal dependence of the $\chi_M T$ for complexes **1** and **2**. Points indicate experimental data and straight lines represent the best fitting curves obtained.

Figure 4.1. Molecular structure of one of the two independent complex cations (A) of **1** with labels of heteroatoms.

Figure 4.2. Molecular structure scheme of the complex cation B of **1** with labels of heteroatoms.

Figure 4.3. The distorted cubane-like core of complex **1**.

Figure 4.4. Layered structure of compound **1** formed by nitrate, 3,5-dicarboxylate pyridine and water molecules connected by H-bonds.

Figure 4.5. 1D coordination polymer of **2** viewed down b axis.

Figure 4.6. Molecular structure of the tetranuclear unit for complex 2, located on a crystallographic two-fold axis. Atom O1 represents the carboxylic oxygen of the bridging phenylenediacrylate anion.

Figure 4.7. Crystal packing of complex **2** highlighting the position of the lattice molecules.

Figure 4.8. Absorption spectra of complexes **1**(red) and **2** (black).

Figure 4.9. Emission spectra of complexes **1**(red) and **2** (black).

Figure 4.10. IR spectrum of complexes **1** (red) and **2** (black).

Figure 4.11. Plot of magnetic susceptibility χ as function of temperature for complex **1** at 0.1 T. The black line represents the model described in the text assuming no free moments, the red line includes a small number of independent s=1⁄2 spins (left-hand scale in SI units and right-hand scale in CGS units).

Figure 4.12. Plot of magnetic susceptibility χ as function of temperature for complex **2** at 0.1 T. The black line represents the model described in the text assuming no free moments, the red line includes a small number of independent s=1/2 spins. Data were taken with field normal to the crystal planes (left-hand scale in SI units and right-hand scale in CGS units).

Figure 4.13. Plot of χT *vs* temperature T for complex **1**, (χ is the linear magnetic susceptibility). The dotted line indicates a system of independent s=1/2 spins with a g-factor=2 (eight Cu^{2+} ions in asymmetric unit of complex **1**). The left-hand scale is in SI units and the right-hand in CGS units.

Figure 4.14. Plot of χT *vs* temperature T for complex **2**, (χ is the linear magnetic susceptibility). The dotted line indicates a system of independent s=1/2 spins with a g-factor = 2 (four Cu^{2+} ions in asymmetric unit of complex **2**). The left hand scale is in SI units and the right-hand in CGS units.

Figure 4.15. Schematic diagrams of (a) the doubly-open cubane-like structure of complex **2**, and of (b) the rectangular tetramer model of antiferromagnetically coupled spins.

Figure 4.16. Magnetization of (a) complex **1** and (b) complex **2** at various temperatures. Circles are experimental data and lines represent the Brillouin function model described above.

Figure 4.17. Cyclic voltammogram of complexes **1** and **2**.

Figure 5.1. Molecular structure of complex **2** with labels of hetero-atoms. The same scheme applies also to complex **1**.

Figure 5.2. Layered structure in crystal packing of complex **1** formed by ClO_4 anions and water molecules connected by H-bonds.

Figure 5.3. Layered structure in crystal packing of compound **2** formed by terephthalate anions and water molecules connected by H-bonds.

Figure 5.4. Electronic spectra of complexes **1** and **2** in methanol**.**

Figure 5.5. Emission spectra of complexes **1** and **2** in methanol**.**

Figure 5.6. IR spectra of complexes **1** and **2.**

Figure 5.7. ESI-MS spectrum of complex **1** (recorded in methanol).

Figure 5.8. ESI-MS spectrum of complex **2** (recorded in methanol).

Figure 5.9. Increase of absorbance around 400 nm after the addition of 100 equiv of 3,5-DTBC to a methanolic solution of complex **1**. The spectra were recorded at intervals of 5 min.

Figure 5.10. Increase in the absorbance around 400 nm after the addition of 100 equiv of 3, 5-DTBC to a methanolic solution of complex **2**. The spectra were recorded at intervals of 5 min.

Figure 5.11. Plot of $\log(A_\infty - A_o)/(A_\infty - A_t)$ vs time for the catalyzed oxidation of 3,5-DTBC with complex **1.**

Figure 5.12. Plot of $\log(A_\infty - A_o)/(A_\infty - A_t)$ vs time for the catalyzed oxidation of 3,5-DTBC with complex **2.**

Figure 5.13. Initial rates *vs* substrate concentration for the 3,5-DTBC to 3,5-DTBQ oxidation reaction catalyzed by complexes **1** and **2** in methanol.

Figure 5.14. Lineweaver-Burk plot of complexes **1** and **2**.

Figure 5.15. ESI-MS spectrum of the 1:100 mixture of complex **1** and 3,5-DTBC (in methanol).

Figure 5.16. ESI-MS spectrum of the 1:100 mixture of complex **2** and 3,5-DTBC (in methanol).

Figure 5.17. Change of the emission spectra of BSA (3 ml, 5.68 µM aqueous solution) upon gradual addition of 10 µL of an aqueous solution (10 µM) of complex **1** at room temperature. The arrow indicates the increase of the complex concentration.

Figure 5.18. Change of the emission spectra of HSA (3 ml, 1.53 µM aqueous solution) upon gradual addition of 10 µL of an aqueous solution (10 µM) of complex **1** at room temperature. The arrow indicates the increase of the complex concentration.

Figure 5.19. Change of emission spectra of BSA (3 ml, 5.68 µM aqueous solution) upon gradual addition of 10 µL of aqueous solution 10 µM of complex **2** at room temperature. The arrow indicates the increase of complex concentration.

Figure 5.20. Change of emission spectra of HSA (3 ml, 1.53 µM aqueous solution) upon gradual addition of 10 µL of aqueous solution 10 µM of complex **2** at room temperature. The arrow indicates the increase of complex concentration.

Figure 5.21. Stern-Volmer plot of complexes **1** and **2** with BSA.

Figure 5.22. Stern-Volmer plot of complexes **1** and **2** with HSA.

Figure 5.23. Change of the electronic absorption spectra of complex **1** (2 ml, 0.19 µM) upon the gradual addition of 10 µL of an aqueous solution (6.66 µM) of CT-DNA. Inset: Plot of [DNA] / $(\varepsilon_a-\varepsilon_f)$ *vs* [DNA]. The arrow shows the changes in absorbance with the increase of DNA concentration.

Figure 5.24. Change of the electronic absorption spectrum of complex **2** (2 ml, 0.19 µM) upon the gradual addition of 10 µL of aqueous solution 6.66 µM of CT-DNA. Inset: Plot of [DNA]/(ε_a-ε_f) *vs* [DNA]. The arrow indicates the increase of DNA concentration.

Figure 5.25. Fluorescence quenching curves of EB bound to CT-DNA upon gradual addition of complex **1** (10 µL, 10 µM). Inset: Stern-Volmer plot of the fluorescence titration.

Figure 5.26. Fluorescence quenching curves of EB bound to CT-DNA upon gradual addition of complex **2** (10 µL, 10 µM). Inset: Stern-Volmer plot of the fluorescence titration.

Figure 5.27. Cyclic voltammograms of complexes **1** and **2** (~ 1×10^{-3} M + 0.1 M NEt_4ClO_4). (Reference electrode: Ag/AgCl. Scan rate: 25 mV/s).