Electronic Supporting Information (ESI) for the manuscript:

Enantioselective self-assembly of antiferromagnetic hexacopper(II) wheels with chiral amino acid oxamates

Thais Grancha, Jesús Ferrando-Soria, Joan Cano, Francesc Lloret, Miguel Julve, Giovanni De Munno,* Donatella Armentano, and Emilio Pardo*

Experimental Section

Materials. All chemicals were of reagent grade quality. They were purchased from commercial sources and used as received.

Physical techniques. Elemental analyses (C, H, N) were performed at the Servicio Central de Soporte a la Investigación (SCSIE) from the Universitat de València (Spain). ¹H NMR spectra were recorded at room temperature on a Bruker AC 200 (200.1 MHz) spectrometer. FT–IR spectra were recorded on a Perkin-Elmer 882 spectrophotometer as KBr pellets. Natural circular dichroism (NCD) curves were recorded using a Jasco model J-810 spectropolarimeter.

HMeEt-(S)-valma and HMeEt-(R)-valma. Both proligands were prepared by following the same synthetic procedure: the hydrochloride forms of the methyl ester derivatives of the corresponding enantiopure amino acids [(L)-valine, 5.0 g, 29.8 mmol (HMeEt-(S)-valma); (D)-valine, 5.0 g, 29.8 mmol (HMeEt-(R)-valma)] were dissolved in 200 mL of dichloromethane and charged with triethylamine (8.3 mL, 59.7 mmol). The resulting colourless reaction mixtures were added dropwise to solutions containing ethyl oxalyl chloride ester (3.3 mL, 29.8 mmol) in dichloromethane (200 mL) under vigorous stirring at 0 °C on an ice-bath and the resulting solutions were further stirred during five hours. The small amount of white solid (Et₃NHCl) formed was filtered off and the resulting solutions were then concentrated in a rotatory evaporator to a final volume of 100 mL. The palid yellow solutions were washed three times with water (3x50 mL) and finally, the solvent was removed in a rotatory evaporator to afford a yellow oil which was further washed with water and dried under vacuum. HMeEt-(S)valma: Yield: 6.7 g, 97%; Anal. calcd (%) for C₁₀H₁₇NO₅ (231.2): C 51.94, H 7.41, N 6.06; found: C 51.87, H 7.29, N 6.06; ¹H NMR ([D₆]DMSO): 0.88 (dd, 6H; 2CH₃ from -CH(CH₃)₂), 1.27 (t, 3H; CH₃ from OCH₂CH₃), 2.15 (m, 1H; CH from -CH(CH₃)₂),

3.65 (s, 3H; OCH₃), 4.15 (dd, 1H; CH), 4.25 (q, 2H; CH₂ from OCH₂CH₃), 9.01 (d, 1H; NH). HMeEt-(*R*)-valma: Yield: 6.4 g, 93 %; Anal. calcd (%) for C₁₀H₁₇NO₅ (231.2): C 51.94, H 7.41, N 6.06; found: C 51.93, H 7.33, N 6.09; ¹H NMR ([D₆]DMSO): 0.88 (dd, 6H; 2CH₃ from –CH(CH₃)₂), 1.26 (t, 3H; CH₃ from OCH₂CH₃), 2.14 (m, 1H; CH from –CH(CH₃)₂), 3.65 (s, 3H; OCH₃), 4.15 (dd, 1H; CH), 4.23 (q, 2H; CH₂ from OCH₂CH₃), 9.01 (d, 1H; NH).

 $(Me_4N)_6\{Cu^{II}_6[(S)-valma])_6\} \cdot 7H_2O (1^S) and <math>(Me_4N)_6\{Cu^{II}_6[(R)-valma])_6\}$ · $7H_2O (1^R)$. A methanolic solution (50 mL) of the corresponding proligand HMeEt-(*S*)-valma or HMeEt-(*R*)-valma (6.2 g, 26.8 mmol) was treated with a 25% methanolic solution of Me₄NOH (39.5 mL, 93.9 mmol). Another methanolic solution (10 mL) of CuCl₂ (3.61 g, 26.8 mmol) was then added dropwise while the reaction mixture was stirred. The resulting deep blue solution was filtered off to remove the small amount of solid particles and then concentrated to dryness in a rotary evaporator. The obtained blue powder was gently washed with acetone and dried under vacuum. Well-formed hexagonal prisms of 1^S and 1^R were grown after several weeks of slow evaporation of a water/methanol solution (1:1 volume ratio) containing the solid. The crystals were collected by filtration and air-dried. Compound 1^S : Yield: 3.7 g, 40 %; Anal.: calcd for C₆₆H₁₃₄Cu₆N₁₂O₃₇ (2069.1): C, 38.31; H, 6.53; N, 8.12%. Found: C, 38.42; H, 6.33; N, 8.13%; IR (KBr): v = 1617 cm⁻¹ (C=O). Compound 1^R : Yield: 3.0 g, 33%; Anal.: calcd for C₆₆H₁₃₄Cu₆N₁₂O₃₇ (2069.1): C, 38.31; H, 6.53; N, 8.12%. Found: C, 38.29; H, 6.40; N, 8.09%; IR (KBr): v = 1618 cm⁻¹ (C=O).

X-ray crystallographic data collection and structure refinement. Singlecrystal X-ray diffraction data of 1^{S} and 1^{R} were collected on a Bruker-Nonius X8APEXII CCD area detector diffractometer using graphite-monochromated Mo-K α radiation at T = 298 K. All calculations for data reduction, structure solution, and refinement were done through the SAINT¹ and SADABS² programs.

The structures were solved by the Patterson method and subsequently completed by Fourier recycling using the SHELXTL software package.³ The final geometrical calculations and the graphical manipulations were carried out with WinGX and CRYSTAL MAKER programs, respectively.^{4,5} All non-hydrogen atoms were refined anisotropically except a carbon atom [C22] of a methyl-ammonium cation highly disordered. The hydrogen atoms of the ligand and those of the methyl-ammonium cations were set in calculated positions and refined as riding atoms while those of the crystallization water molecules were not defined.

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 931371–931372.

. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK [fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk].

Magnetic measurements. Variable-temperature (2.0–300 K) direct current (dc) magnetic susceptibility measurements under an applied field of 100 (T < 30 K) and 10000 G ($T \ge 30$ K) were performed with a Quantum Design SQUID magnetometer for polycrystalline samples of 1^8 and 1^R . In order to confirm the stability of the hexacopper(II) wheels in solution, variable-temperature (2.0–150 K) direct current (dc) magnetic susceptibility measurements of a frozen methanolic solution of 1^8 were also

¹ SAINT, version 6.45, Bruker Analytical X-ray Systems, Madison, WI, 2003.

² G.M. Sheldrick, SADABS Program for Absorption Correction, version 2.10, Analytical X-ray Systems, Madison, WI, 2003.

³ SHELXTL, Bruker Analytical X-ray Instruments, Madison, WI, 1998.

⁴ L.J. Farrugia, J. Appl. Cryst., 1999, 32, 837.

⁵ D. Palmer, CRYSTAL MAKER, Cambridge University Technical Services, Cambridge, 1996.

carried out under an applied field of 100 (T < 30 K) and 5000 G ($T \ge 30$ K). The magnetic susceptibility data were corrected for the diamagnetism of the constituent atoms, as well as for the temperature-independent paramagnetism [$60 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$ per one copper(II) ion] and the sample holder.

Spectroscopic measurements. Q-band EPR spectra ($\nu = 34.277$ GHz) of polycrystalline powdered samples and frozen methanolic solutions of 1^{S} and 1^{R} were recorded in non-saturating conditions at 60 K on a Bruker ER 200 D spectrometer equipped with a helium cryostat.

Table S1. Crystal data and structure refinement for 1^s.

Empirical formula	$C_{66}H_{134}Cu_6N_{12}O_{37}$	
Formula weight	2069.09	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Hexagonal	
Space group	<i>P</i> 6(3)	
Unit cell dimensions	a = 16.8745(7) Å	α= 90°.
	b = 16.8745(7) Å	β=90°.
	c = 21.0124(14) Å	$\gamma = 120^{\circ}$.
Volume	5181.6(5) Å ³	
Ζ	2	
Density (calculated)	1.326 Mg/m ³	
Absorption coefficient	1.288 mm ⁻¹	
<i>F</i> (000)	2168	
Crystal size	0.30 x 0.28 x 0.24 mm ³	
Theta range for data collection	1.39 to 23.06°.	
Index ranges	-18<= <i>h</i> <=18, -18<= <i>k</i> <=18, -23<= <i>l</i> <=23	
Reflections collected	61429	
Independent reflections	4858 [R(int) = 0.0365]	
Completeness to theta = 23.06°	99.8 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4858 / 12 / 361	
Goodness-of-fit on F^2	1.156	
Final <i>R</i> indices $[I > 2\sigma(I)]$	R1 = 0.0595, wR2 = 0.1629	
R indices (all data)	R1 = 0.0731, wR2 = 0.1842	
Absolute structure parameter	-0.02(2)	
Extinction coefficient	0.0068(10)	
Largest diff. peak and hole	0.920 and -0.570 e Å ⁻³	

 ${}^{a}R_{1} = \sum (|F_{o}| - |F_{c}|) / \sum |F_{o}|. {}^{b}wR_{2} = \left[\sum w(F_{o}^{2} - F_{c}^{2})^{2} / \sum w(F_{o}^{2})^{2}\right]^{1/2}. {}^{c}S = \left[\sum w(|F_{o}| - |F_{c}|)^{2} / (N_{o} - N_{p})\right]^{1/2}.$

Table S2. Crystal data and structure refinement for 1^R.

Empirical formula	$C_{66}H_{134}Cu_6N_{12}O_{37}$	
Formula weight	2069.09	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Hexagonal	
Space group	<i>P</i> 6(3)	
Unit cell dimensions	a = 16.7208(4) Å	α= 90°.
	b = 16.7208(4) Å	β=90°.
	c = 20.8549(8) Å	$\gamma = 120^{\circ}$.
Volume	5049.5(3) Å ³	
Z	2	
Density (calculated)	1.361 Mg/m ³	
Absorption coefficient	1.321 mm ⁻¹	
<i>F</i> (000)	2168	
Crystal size	0.28 x 0.20 x 0.18 mm ³	
Theta range for data collection	1.41 to 23.30°.	
Index ranges	-18<= <i>h</i> <=18, -18<= <i>k</i> <=18, -23<= <i>l</i> <=23	
Reflections collected	60872	
Independent reflections	4882 [R(int) = 0.0285]	
Completeness to theta = 23.30°	99.9 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4882 / 12 / 358	
Goodness-of-fit on F ²	1.144	
Final <i>R</i> indices $[I > 2\sigma(I)]$	R1 = 0.0611, wR2 = 0.1637	
R indices (all data)	R1 = 0.0745, wR2 = 0.1831	
Absolute structure parameter	-0.01(2)	
Extinction coefficient	0.0065(9)	
Largest diff. peak and hole	0.933 and -0.598 e Å ⁻³	

 ${}^{a} R_{1} = \sum (|F_{o}| - |F_{c}|) / \sum |F_{o}|. {}^{b} w R_{2} = \left[\sum w (F_{o}^{2} - F_{c}^{2})^{2} / \sum w (F_{o}^{2})^{2}\right]^{1/2}. {}^{c} S = \left[\sum w (|F_{o}| - |F_{c}|)^{2} / (N_{o} - N_{p})\right]^{1/2}.$



Fig. S1 Perspective view of the asymmetric unit of 1^S [symmetry code: (a) = -*y*, *x* - *y*, *z*] (left) and 1^R [symmetry code: (a) = -*x* + *y*, -*y*, *z*] (right) with the atom numbering scheme. Selected bond distances (Å) and interbond bite angles (°): Cu(1)–N_{eq} = 1.905(5) (1^S)/1.891(5) (1^R), Cu(2)–N_{eq} = 1.912(5) (1^S)/1.894(5) (1^R), Cu(1)–O_{eq} = 2.001(5) (1^S)/1.969(5) (1^R), Cu(2)–O_{eq} = 1.987(5) (1^S)/1.984(4) (1^R), Cu(1)–O_{ax} = 2.260(5) (1^S)/2.241(5) (1^R), Cu(2)–O_{ax} = 2.398(5) (1^S)/2.367(5) (1^R); N_{eq}–Cu(1)–O_{eq} = 82.8(2) (1^S)/83.4(2) (1^R), N_{eq}–Cu(1)–O_{eq} = 83.7(2) (1^S)/82.8(2) (1^R), O_{eq}–Cu(1)–O_{ax} = 78.0(2) (1^S)/80.6(2) (1^R).



Fig. S2 Projection view of the crystal packing of 1^{R} along the crystallographic *c* axis. The carbon, nitrogen and oxygen atoms from the hexanuclear copper(II) wheels are shown as grey sticks whereas the copper atoms are depicted as green polyhedra. The tetramethylammonium countercations are shown as spheres with the real atomic radius. The water molecules have been omitted for clarity.



Fig. S3 Perspective views of the bowl-like hexacopper(II) rings of 1^{s} (a and c) and 1^{R} (b and d) with the templating tetramethylammonium cation. The hexanuclear rings are drawn as grey sticks whereas the tetramethylammonium countercations are shown as spheres with arbitrary radii. The crystallization water molecules have been omitted for clarity.



Fig. S4 Schematic views along the crystallographic c axis of the hexacopper(II) rings of 1^{s} (left) and 1^{R} (right) showing the pseudo-helicoidal motif of the supramolecular assemblies.

Electronic Supplementary Material (ESI) for Chemical Communications This journal is C The Royal Society of Chemistry 2013



Fig. S5 View along the crystallographic b axis of the wheel 1^{s} showing the plane of the crystallization water molecules linked with hydrogen bonds to the walls of the wheel.



Fig. S6 Temperature dependence of χ_M (\circ) and $\chi_M T$ (\bullet) for $\mathbf{1}^{\mathsf{R}}$ under applied dc fields of 100 G (T < 30 K) and 10 kG ($T \ge 30$ K). The solid lines correspond to the best-fit curves (see text).



Fig. S7 Temperature dependence of $\chi_M T(\mathbf{O})$ for a methanolic solution of $\mathbf{1}^{s}$ under applied dc fields of 100 G (T < 30 K) and 1000 G ($T \ge 30$ K). The inset shows the maximum of χ_M (\bigcirc) for $\mathbf{1}^{s}$ in the low-temperature region.



Fig. S8 Q-band EPR spectra of polycrystalline samples of $\mathbf{1}^{s}$ (a) and $\mathbf{1}^{R}$ (b) at 60 K.



Fig. S9 Q-band EPR spectra of frozen methanolic solutions of 1^{s} (a) and 1^{R} (b) at 60 K.