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for

A pH-triggered bistable copper(II) metallacycle as reversible emulsion switch for biphasic processes

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1. Experimental Section

1.1. General methods. All the reactants were from analytical grade and they were used without further purification. Elemental analysis (C, H and N) was performed with a Perkin-Elmer 2400 analyser. Atomic absorption for Cu was performed with a Hitachi Z-8200 Polarized Atomic Absorption Spectrophotometer. Infrared spectra were recorded with a Perkin-Elmer GX FTIR spectrophotometer in the range 4000 - 400 cm⁻¹ by using KBr pellets. The pH measurements were performed on an Oakaton instrument in the 0.00 -14.00 range with a resolution of 0.01 units of pH at room temperature. UV-Vis spectra were done with a Shimadzu UV 2550 spectrometer. Photographs were taken using 8.0 megapixel camera from Samsung Galaxy II mobile phone. ¹H and ¹³C NMR spectra were obtained at room temperature (RT) with a Bruker DPX-200 Avance (¹H: 200 MHz, ¹³C: 50 MHz) spectrometer using dimethyl sulfoxide (dmso-d₆) as the solvent and tetramethylsilane (TMS) as the internal reference. The ¹³C signals due to <u>CH/CH₃ and CH₂ were assigned according to the DEPT 135 ¹³C-NMR spectra.</u> Multiplicities are indicated by s (singlet), d (doublet), t (triplet) and q (quartet).

Cyclic voltammetry was performed by using a three-electrode cell and a PG29 Omnimetra potentiostat. Platinum was the working electrode, Ag/AgCl with KCl saturated was the reference electrode and a platinum wire was used as counter electrode. The supporting electrolyte was KClO₄ 10^{-3} mol L⁻¹. Cyclic voltammograms were collected over the range 50 – 300 mV s⁻¹ in acetonitrile and water with pH = 1.0 and 11.0 at 25 °C. The solutions were deoxygenated with argon during 15 min prior each experiment. The peak-to-peak separations (ΔE_p) of the copper pairs in acetonitrile, were similar to that of the ferroceniumferrocene couple under the same conditions, i.e. around 160 mV. Each scan started at the maximum potential. All formal potentials were referred to the saturated calomel electrode (SCE). Gas chromatography with FID detector (Carbowax column -Shimadzu GC17A) was used to monitor the disappearance of quinoline in the oil phase. Electrospray ionization mass spectrometry ESI-MS was performed in an ION-TRAP LCQFleet (ThermoScientific) in negative and positive modes to verify the structure of the complexes in solution. The reaction samples were analyzed by introducing aliquots into the ESI source with a syringe pump at a flow rate of 15 µL min⁻¹. The spectral data obtained were averaged for five scans at 0.2 s each one. Typical ESI conditions used a heated capillary temperature of 275 $^{\circ}$ C, sheath gas (N₂) at a flow rate of 15 units (ca. 4 L min⁻¹), a spray voltage of 2 kV, a capillary voltage of 25 V and a tube lens offset voltage of 25 V. The d.c. magnetic measurements were performed with a SQUID Cryogenic S600 magnetometer. The diamagnetic corrections for the constituent atoms were estimated from Pascal's tables. Corrections for the temperature-independent paramagnetism [60 x 10⁻⁶ cm³ mol⁻¹ per copper(II) ion] as well as for the sample holder were also applied.

Microscopy images were performed on a microscope Opton model TNB-41T-PL.

1.2. Synthesis and crystal data

Synthesis of the proligand. Et₂H₂L: Triethylamine 99% (37.4 mmol, 5.24 mL) and ethyloxalyl chloride 98% (37.4 mmol, 4.24 mL) were added dropwise to a tetrahydrofurane solution (400 mL) containing 2,2'-ethylenedianiline (18.8 mmol, 4.0 g) at 10 °C. The resulting mixture was brought to reflux at 65 °C for 3 h. After this time, the white precipitate of Et₃NHCl was removed by filtration and the resultant solution was concentrated on a rotary evaporator until the formation of a yellow oil. A small volume of ice-cold distilled water was added to precipitate a yellow solid which was filtered, washed with water and dried under vacuum into a desiccator for 5 h. Yield: 7.076 g, 91 %. IR (KBr): 3399 (vNH), 2982, 2876 (vCH), 1763, 1715 (vC=O), 1587, 1526 cm⁻¹ (vC=C). ¹H NMR (200 MHz, DMSO-d₆, 25°C, TMS, δ): 1.32 (t, 6 H, CH₃), 2.77 (s, 4 H, CH₂), 4.36 (q, 4 H, CH₂), 7.28 (d, 4 H, Ar-H), 10.35 ppm (s, 2 H, NH). ¹³C NMR (200 MHz, DMSO-d₆, TMS, δ): 14.24 (C₁₁), 31.57 (C₉), 62.72 (C₁₀), 126.95 (C₅), 127.24 (C₇), 129.83 (C₅,C₈), 134.62 (C₃), 137.18 (C₄), 156.88 (C=O), 161.27 ppm (C=O).

Synthesis of the complexes. $[Cu_2(H_2L^{anti})_2(EtOH)_2]$ •2EtOH (1): Aqueous 20% w/v of Et₄NOH (0.5 mmol, 0.37 mL) was poured into a solution containing the Et₂H₂L proligand (1.0 mmol, 412.44 mg) dissolved in 50.0 mL of ethanol and 25.0 mL of water under vigorous stirring at 40 °C for 40 min. The system was cooled to 4 °C and then, Cu(NO₃)₂ • 3H₂O (1.0 mmol, 241.6 mg) previously dissolved in 5.0 mL of water was added dropwise under continuous stirring. The system was heated to 60 °C for 5 min and then allowed to cool at room temperature. The insoluble green solid (most likely an unwanted polymerisation product) was removed by filtration and the mother liquor left in the refrigerator at ca. 5 °C. Pale green parallelepipeds of 1 were grown after two weeks. They were collected by filtration and dried on filter paper. Yield: 34 % (172.52 mg). Anal. calcd. for C₄₄H₅₂Cu₂N₄O₁₆ (1) M_r = 1019.98 g mol⁻¹: C 51,91; H 4.93; N 5.50; Cu 12.48. Found: C 50.90; H 4.88; N 5.65; Cu 12.50 %. IR (KBr): 3348 (vNH), 3065, 2933, 2866 (vCH), 1702, 1687, 1669, 1639 (vC=O), 1587, 1510 cm⁻¹ (vC=C).

 $[Bu_4N]_4[Cu_2(L^{gauche})_2]$ •4H₂O (2): To a solution containing the Et₂H₂L proligand (7.2 mmol, 3.00 g) dissolved in 220 mL of ethanol and 110 mL of water, aqueous 40% w/v Bu₄NOH (28.9 mmol, 18.72 mL) was added under vigorous stirring at 60 °C for 30 min. The system was cooled at room temperature and an aqueous solution (30 mL) of CuCl₂•2H₂O (7.2 mmol, 1.22 g) was added dropwise under continuous and vigorous stirring. The resulting olive green solution was filtered to remove a small amount of solid particles and the mother liquor was concentrated in rotary evaporator until the formation of a dark green oil. It was dissolved in dichloromethane and washed several times with small portions of distilled water until the chloride test with AgNO₃ was negative. The dichloromethane solution was totally evaporated and the residue washed with acetone to afford an olive green solid that was filtered and air dried. Yield: 31 % (4.019 g). Supernatant acetone containing small amount of dissolved green product was poured into a glass crystallizer covered with parafilm® and left in the refrigerator at 5 °C. X-ray quality dark green prismatic crystals of 2 were grown after two weeks. Anal. calcd. for $C_{100}H_{164}Cu_2N_8O_{16}$ (2), Mr = 1861.47 g mol⁻¹: C 64.10; H 9.47; N 5.98; Cu 6.78. Found: C 65.08; H 9.41; N 6.11; Cu 7.07 %. IR (KBr): 3439 (vOH), 2959, 2939, 2873s (vCH), 1644, 1617 (vC=O), 1588, 1480 (vC=C), 1302 cm⁻¹ (vC=N).

Crystal data. 1: $C_{44}H_{52}Cu_2N_4O_{16}$, M_r =1019.98, triclinic, space group *P*-1, *a* = 8.82221(2), *b* = 11.5730(3), *c* = 13.5452(3) Å, α = 68.274(2), β = 86.530(2), γ = 82.154(2)°, *V* = 1272.60(5) Å³, *T* = 120(2) K, *Z* = 1, ρ_{calcd} = 1.331 g cm⁻³, 34911 unique reflections, and 5755 observed with *I* > 2 σ (*I*), final *R*1 = 0.0684, *wR*2 = 0.2306. **2**: $C_{100}H_{164}Cu_2N_8O_{16}$, M_r = 1861.47, orthorhombic, space group *I*222, *a* = 14.2234(2), *b* = 17.5944(4), *c* = 21.3698(4) Å, *V* = 5347.84(17) Å³, *T* = 293 K, *Z* = 2, ρ_{calcd} = 1.196 g cm⁻³, 55826 unique reflections, and 5208 observed with *I* > 2 σ (*I*), final *R*1 = 0.049, *wR*2 = 0.1443. Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no CCDC-927507 (Et₂H₂L), CCDC-927505 (1, [Cu₂(H₂L)₂],) and CCDC-927506 (**2**, [Cu₂L₂]⁴). Copies of these data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif.

1.3. Stability of the complex under variation of pH

The UV-Vis spectrum was recorded at the 484 nm on a solution of **2** (25.6 mg, 1.5 mL) dissolved in deionized water and it exhibited a maximum at 634 nm. Then an aqueous solution containing NaOH (10 μ L, 6.0 mol L⁻¹) was added to shift the pH to the basic media, and UV-Vis spectrum was also recorded, showing the same value of the maximum of the absorbance at 634 nm. After that, an aqueous solution of (20 μ L) HCl (6.0 mol L⁻¹) was added to form complex **1**, and the UV-Vis was also recorded. The maximum of the absorbance is then shifted to 714 nm. This procedure was repeated for 30 times, the maximum exactly at the same value obtained at the first time (i.e., 684 nm), being observed at the end in the UV-Vis spectrum for compound **2**. This clearly supports the reversibility of the equilibrium in aqueous solution.

1.4. Emulsion formation and breaking of water-cyclohexane mixtures containing the complex

This experiment was done as follows: 1.5 mL of cyclohexane was added to a solution of 1 (25.6 mg, 1.5 mL) in deionized water previously poured into a quartz cuvette, and the system was stirred until the formation of a stable emulsion. The absorbance at 480 nm was monitored at intervals of 1 s during 1000 s. This high value of absorbance obtained is probably due to the scattering of the radiation caused by the emulsion containing several droplets of cyclohexane dispersed in water, confirming the high stability of the emulsion. Then an aqueous solution containing NaOH (10 μ L, 6.0 mol L⁻¹) was added followed by stirring for about 1 s, leading to the immediate breaking of the emulsion and consequent decrease of the radiation scattering. The process may occur for several cycles as shown in the main text, just by modifying the pH value.



Fig. S1 Microscope images showing the (a) emulsionated and (b) demulsionated states.

1.5. Quinoline oxidation tests

An aqueous solution of 2 (5 mL, 0.047 mmol) and 500 μ L of H₂O₂ (30% in water) were poured into a solution containing quinoline dissolved in cyclohexane (5 mL, 500 ppm). This mixture was prepared twice to perform both the acid and basic catalytic tests. To study the oxidation of the quinoline in acid media, an aqueous solution of HCl (500 μ L, 1.0 mol L⁻¹) was added. In a similar way, in the second beaker containing the quinoline, an aqueous solution of NaOH (500 μ L, 2.0 mol L⁻¹) was added for the basic test. A blank containing only quinoline in cyclohexane, water and H₂O₂ in the same conditions described was also prepared and used immediately.

2. Crystal structure determinations

Single crystals of the Et₂H₂L proligand and the complexes **1** and **2** were mounted on polyamide samples holding and used for data collection. X-ray diffraction measurements were performed on an Oxford-Diffraction GEMINI-Ultra diffractometer using graphite-monocromated source Mo-K α radiation ($\lambda = 0.71069$ Å) at 120(10) (Et₂H₂L and **1**) and 293(2) K (**2**). Data integration and scaling of the reflections were performed with the CRYSALIS suite¹. Final unit cell parameters were based on the fitting of all reflections positions. The structures were solved by direct methods using the program SUPERFLIP² and refined by full-matrix least-squares techniques against F^2 using SHELXL-97³. Positional and anisotropic atomic displacement parameters were refined for all non-hydrogen atoms.

Ethanol in 1 and crystallization water molecules in 2 were found to be disordered and refined with split atomic positions. A continuous negative density was found in the difference map in the large void for the molecular structure of compound 1 (1272.6 $Å^3$) suggesting the presence of free solvent molecules. The disordered refined model considers only an ethanol molecule over this region.

Hydrogen atoms close to carbon atoms were located in difference maps, included in idealized positions and refined according to the riding model approximation⁴. Molecular graphics were produced with the ORTEP^{4,5} and Mercury® programs⁶. A summary of the crystal data, experimental details and refinement results is given in Table 1. Crystallographic data for the structures reported in this contribution were deposited with the Cambridge Crystallographic Data Centre as supplementary publication n^o CCDC-927507 (Et₂H₂L), CCDC-927505 (**1**, $[Cu_2(H_2L)_2]$,) and CCDC-927506 (**2**, $[Cu_2L_2]^4$). These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www. ccdc.cam.ac.uk/data_request/cif.



Fig. S2 Representation of the Et_2H_2L proligand with the atom-numbering scheme. Thermal ellipsoids are drawn at the 50% probability level. Symmetry code: (a) =1-x, 1-y, 1-z.



Fig. S3 View of the asymmetric unit of **1** with the atom-numbering scheme. Thermal ellipsoids are drawn at the 50% probability level.



Fig. S4 View of the dinuclear unit of 2 with the atom-numbering scheme. Water and tetrabutylammonium molecules were omitted for sake of clarity. Displacement atomic parameters are drawn at the 50 % probability level. Symmetry code: (*a*) = 2-x, 2-y, 2; (*b*) = x, 2-y, 2-z; (*c*) = 2-x, y, 2-z.

	Et_2H_2L	1	2
formula	$C_{22}H_{24}N_2O_6$	$C_{44}H_{52}Cu_2N_4O_{16}$	$C_{100} H_{164} Cu_2 N_8 O_{20}$
$M_r [\mathrm{g} \;\mathrm{mol}^{-1}]$	412.43	1019.98	1861.47
crystal system	Monoclinic	Triclinic	Orthorhombic
space group	$P2_1/c$	<i>P</i> –1	1222
Temperature [K]	120	120	293
<i>a</i> [A]	6.6560 (2)	8.8221 (2)	14.2234 (2) Å
<i>b</i> [Å]	9.1479 (2)	11.5730 (3)	17.5944 (4) Å
<i>c</i> [Å]	16.3406 (4)	13.5452 (3)	21.3698 (4) Å
α [°]	90	68.274 (3)	90
β [°]	93.502 (2)	86.530 (19)	90
γ[°]	90	82.154 (2)	90
<i>V</i> [Å ³]	993.10(4)	1272.60(5)	859.5(3)
Z	2	1	2
λ [Å]	0.71073	0.71073	0.71073
$ ho_{ m calcd} [{ m g \ cm}^{-3}]$	1.379	1.331	1.156
$\mu \ [\mathrm{mm}^{-1}]$	0.10	0.90	0.46
F(000)	436	530	2012
crystal size	0.58 x 0.18 x 0.12	$0.55\times0.24\times0.12$	$0.42\times0.39\times0.38$
θ range [°]	2.4–26.4	2.8-31	1.8–29.5
h, k, l ranges	-8 to 8,	-11 to 11,	-17 to 17,
	-11 to 11,	-14 to 14,	-21 to 21,
	-20 to 20	-16 to 16	-26 to 26
reflns collected	12200	30924	55826
Ind. reflns (R_{int})	2039	5199	5497
$R1^{[a]}[I > 2\sigma(I)]$	0.033	0.076	0.049
$wR_2^{[0]}[I > 2\sigma(I)]$	0.089	0.247	0.176
	1.09	1.08	0.84
Residuals [e A ⁻³]	0.25, -0.18	2.73, -1.82	1.30, -0.39

Table S1. Crystal data and structure refinement for the Et₂H₂L proligand and complexes 1 and 2

[a] $R_1 = \sum (jF_oj - jF_cj) / \sum jF_oj.$ [b] $wR_2 = [\sum w(jF_oj - jF_cj)^2 / \sum wjF_oj^2]^{1/2}.$

where

where $W = 1/[\sigma^2(F_o^2) + (0.0472P)^2 + 0.1497P]$ where $P = (F_o^2 + 2F_c^2)/3$. $W = 1/[\sigma^2(F_o^2) + (0.1625P)^2 + 4.4469P]$ where $P = (F_o^2 + 2F_c^2)/3$. $W = 1/[\sigma^2(F_o^2) + (0.1781P)^2 + 5.8980P]$ where $P = (F_o^2 + 2F_c^2)/3$.

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Cu1—O1	1.945 (3)
Cu1—O7	1.948 (3)
Cu1—O4	1.973 (3)
Cu1—O2	1.994 (3)
Cu1—O4 ⁱ	2.365 (3)
Cu1—O5	2.426 (3)
01—Cu1—O7	91.83 (14)
01—Cu1—O4	174.58 (12)
O7—Cu1—O4	93.45 (13)
O1—Cu1—O2	84.43 (13)
O7—Cu1—O2	174.90 (13)
O4—Cu1—O2	90.22 (13)
O1—Cu1—O4 ^a	103.25 (13)
O7—Cu1—O4 ^a	96.82 (13)
O4—Cu1—O4 ^a	77.34 (13)
O2—Cu1—O4 ⁱ O4 ^a	87.44 (12)
O1—Cu1—O5	102.05 (13)
O7—Cu1—O5	94.70 (13)
O4—Cu1—O5	76.30 (12)
O2—Cu1—O5	82.72 (12)
O4 ^a —Cu1—O5	151.76 (11)
C2—O2—Cu1	109.8 (3)
C18—O4—Cu1	119.1 (3)
C18—O4—Cu1 ^a	130.2 (3)
Cu1—O4—Cu1 ^a	102.65 (13)
C1—O1—Cu1	113.6 (3)
C17—O5—Cu1	101.0 (3)
Н9А—С9—Н9В	107.6
O6-C18-O4	127.3 (4)
O6-C18-C17	117.8 (4)
O4—C18—C17	114.8 (4)
C3—C8—C7	119.6 (4)
С3—С8—Н8	120.2
С7—С8—Н8	120.2
С11—С10—С9	110.8 (3)
C11—C10—H10A	109.5
С9—С10—Н10А	109.5
C11—C10—H10B	109.5
C9—C10—H10B	109.5

Table S2.Selected bonds and distances relative to Cu atoms(Å, deg) for 1^{\ast}

*Symmetry code: (a) -*x*+1, -*y*, -*z*.

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Cu1—N1 ^c	1.939 (2)	
Cu1—N1	1.939 (2)	
Cu1—O1 ^c	1.948 (2)	
Cu1—O1	1.948 (2)	
N1 ⁱ —Cu1—N1	158.29 (14)	
N1 ⁱ —Cu1—O1 ^c	84.10 (10)	
N1—Cu1—O1 ^c	99.26 (9)	
N1 ⁱ —Cu1—O1	99.26 (9)	
N1—Cu1—O1	84.09 (9)	
01°-Cu1-O1	162.27 (14)	
C1	113.63 (18)	
C2—N1—C3	119.4 (2)	
C2—N1—Cu1	114.27 (19)	
C3—N1—Cu1	126.18 (18)	

Table S3.Selected bonds and distances relative to Cu atoms(Å, deg) for compound 2*

*Symmetry code: (a) = 2-x, 2-y; z(b) = x, 2-y, 2-z; (c) = 2-x, y, 2-z



3. Solution UV-Vis spectra for 1 and 2

Fig. S5 (a) Reversible interconversion of **1** and **2** in aqueous solution by the pH change from 5.0 to 10.0 in 30 consecutive cycles. The cycles were evaluated by UV/Vis. The inset shows the absorption maximum of **2** (pH = 10.0) in the first and in the thirty pH variation cycle. The small differences observed in this curve are due to the dilution. (b) Solution UV-Vis spectra of the equilibrium involving complexes **1** and **2** at pH values of 5.0 and 10.0. The pH of the aqueous medium was controlled by the addition of small portions of an aqueous solution of NaOH (0.1 mol L⁻¹) to the solution of **1** (0.02 mol L⁻¹) in order to reach the value of 10.0. After that, small amounts of an aqueous solution of HCl (0.1 mol L⁻¹) were added to render the pH equal to 5.0.

The stability of the species and the reversibility of the equilibria shown in equation (1) (see main text) have been demonstrated in a 30 cycles experiment (Fig. S5a) by varying the pH value of an aqueous solution of $[Cu_2L_2]^{4-}$ in the range 5.0-10.0 (Fig. S5b).



Fig. S6 UV-Vis spectra recorded at pH values of 3.0, 5.0, 7.0, 9.0, 10.0 and 13.0. The aqueous solution of **2** has a pH value of 5.0. The pH of the aqueous solutions of **2** (0.02 mol L^{-1}) was controlled by addition of small portions of an aqueous solution of NaOH (0.1 mol L^{-1}) to reach the values of 7.0, 9.0, 10.0 and 13.0. After that, small amounts of an aqueous solution of HCl (0.1 mol L^{-1}) were added to decrease the pH value to 3.0.

4. ESI-MS spectra of 1 and 2

 $\begin{bmatrix} Cu_2(H_2L)_2 \end{bmatrix} \longleftrightarrow \begin{bmatrix} (Cu_2HL)(H_2L) \end{bmatrix}^{-} \Leftrightarrow \begin{bmatrix} Cu_2(H_2L)_2 \end{bmatrix}^{2-} \Leftrightarrow \begin{bmatrix} Cu_2L_2 \end{bmatrix}^{4-}$ Lower pH $\frac{m/z 833}{m/z 417} \qquad \frac{m/z 207}{Higher pH}$

(b)

(a)



Fig. S7 (a) Schematic reaction showing the main existing species in solution. (b) ESI-MS in the negative-ion mode of an aqueous solution containing the complexes at pH values of 3.0, 5.0 and 10.0. Diluted solutions of NaOH and HCl were used to shift the pH to the desired values.

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4. Emulsions in different media



(a) (b) Fig. S8 Emulsions containing 1 as metallosurfactant in (a) water-gasoline and (b) water-soya bean oil.

5. Kinetics of quinoline oxidation monitored by GC-FID in the presence of 1, HCl and H₂O₂



Fig. S9 Monitoring the quinoline peak disappearance in the oil phase during the reaction in acid medium by GC-FID. During the reaction in acid medium, aliquots of oil phase were injected at determined times into a GC with FID detector. Figure S9 shows the disappearance of the quinoline peak, due to its oxidation and subsequent extraction into the aqueous phase.

6. UV-Vis spectra in the presence of 1, HCl and H₂O₂



Fig. S10. Eletronic spectra of 1 in the aqueous phases before (left, black curve), during (right, red curve) and after (middle, green curve) the activation of 1 with H_2O_2 .



7. Preliminary cyclic voltammetry experiments

Fig. S11 Cyclic voltammogram (CV) of 1 in water at pH = 3.0 and 300 mV s⁻¹.



Fig. S12 (Red) Cyclic voltammogram (CV) of **2** in water and 300 mV s⁻¹. (Blue) CV of **2** in acetonitrile at 50 mV s⁻¹ is shown for comparison.

1 exhibits two rather well-separated irreversible, redox waves in water (pH = 3.0), with anodic oxidation peaks at $E_{1a} = +0.08$ V and $E_{2a} = +0.35$ V vs. SCE together with the corresponding cathodic reduction peaks at $E_{1c} = -0.21$ V and $E_{1c} = +0.14$ V vs. SCE (Fig. S11). The two anodic peaks can be attributed to the successive oxidation of each metal center, formally two oneelectron Cu^{II}–Cu^{III} couples, indicating thus that the dinuclear nature of complex **1** is kept in acidic aqueous solution. Moreover, the relatively large separation between these two oxidation peaks ($\Delta E_{1/2} = E_{2a} - E_{1a} = 265$ mV) indicates that the electronic interaction between the metal centers through the double monoatomic oxo(carboxylate) bridges is important (see the discussion of the magnetic properties).

2 exhibits instead a poorly reversible, single redox wave in water (pH = 11.0), with an anodic oxidation peak at $E_a = +0.18$ V and a cathodic reduction peak at $E_{1c} = -0.11$ V vs. SCE. The anodic peak can be attributed to the simultaneous oxidation of the two non-interacting metal centers, formally a two-electron Cu^{II}–Cu^{III} pair, as expected from the rather long intermetallic distance (Cu–Cu = 6.591 Å) across the multiatom diphenylethylene bridges (see also the discussion of the magnetic properties). The cathodic peak of lower intensity is then assigned to the reduction of the decomposition products resulting from coupled chemical reactions in basic aqueous media. More probably, they would correspond to the copper(III)-promoted ligand hydrolysis by OH⁻ groups to yield the corresponding oxalate and/or diamine complexes, as previously reported for related mononuclear copper(II) complexes with aromatic-substituted bis(oxamate) ligands⁷. This is supported by the CV of **2** in (non-aqueous neutral) acetonitrile solution, which exhibits a single pseudo-reversible oxidation wave with an anodic oxidation peak at $E_a = +0.66$ V and a cathodic reduction peak at $E_c = +0.49$ V vs. SCE (Fig. S12). In fact, the peak-to-peak separation ($\Delta E_p = E_a - E_c = 170$ mV) is similar to that of the ferrocenium–ferrocene couple which is stated to be reversible under the same conditions [ΔE_p (Fe⁺/Fc) = 170 mV].

8. Preliminary magnetic measurements and discussion

Variable-temperature (2.0–300 K) magnetic susceptibility measurements were carried out with a SQUID magnetometer under an applied field of 10 kOe ($T \ge 50$ K) and 100 Oe (T < 50 K). The experimental data were corrected for the diamagnetic contributions of the constituent atoms and the sample holder as well as for the temperature-independent paramagnetism (tip) of the Cu^{II} ion (60×10^{-6} cm³ mol⁻¹).



Fig. S13. Temperature dependence of the $\chi_M T$ product of 1 (o) and 2 (Δ). The solid lines represent the best-fit curves (see text).

The magnetic properties of **1** and **2** under the form of $\chi_M T vs. T$ plots [χ_M being the magnetic susceptibility per dicopper(II) unit and *T* the absolute temperature] are shown in Figure S13. At room temperature, the values of $\chi_M T$ are 0.83 (**1**) and 0.77 cm³ mol⁻¹ K (**2**). They are as expected for two magnetically isolated Cu^{II} ions [$\chi_M T = 2 \times (N\beta^2 g_{Cu}^2/3k_B)S_{Cu}(S_{Cu} + 1)$ = 0.83 cm³ mol⁻¹ K (**2**). They are as expected for two magnetically isolated Cu^{II} ions [$\chi_M T = 2 \times (N\beta^2 g_{Cu}^2/3k_B)S_{Cu}(S_{Cu} + 1)$ = 0.83 cm³ mol⁻¹ K with $S_{Cu} = \frac{1}{2}$ and $g_{Cu} = 2.1$, where *N*, β and k_B have their usual meaning]. Upon cooling, $\chi_M T$ increases smoothly for **1** to reach a value of 1.05 cm³ mol⁻¹ K at 2.0 K. This magnetic behaviour reveals the occurrence of a moderately weak ferromagnetic interaction between the two Cu^{II} ions across the out-of-plane double oxo(carboxylate) bridge. $\chi_M T$ for **2** remains practically constant down to *ca*. 8.0 K and then it decreases slightly to reach a value of 0.66 cm³ mol⁻¹ K at 2.5 K. This magnetic behaviour can be attributed to a very weak antiferromagnetic interaction between the two Cu^{II} ions through the extended 2,2'-ethylenediphenylenediamidate bridges and/or non-negligible intermolecular antiferromagnetic interactions. The magnetic susceptibility data of 1 and 2 were analyzed by means of a modified Bleaney-Bowers expression⁷ for two magnetically interacting spin doublets derived through the spin Hamiltonian $H = -J S_1 \cdot S_2$ (with $S_1 = S_2 = S_{Cu} = 1/2$) in which weak intermolecular magnetic interactions through the mean field approximation have been considered [Eq. (S.1)].

$$\chi_{\rm M} = [2N\beta^2 g_{\rm Cu}^2 / k_{\rm B}(T - \theta)] / [3 + \exp(-J/kT)] \qquad \text{Eq. (S.1)}$$

In this expression *J* is the magnetic coupling parameter, g_{Cu} is the Landé factor of the Cu^{II} ions, and θ is the Weiss factor defined as $\theta = zjS_{Cu}(S_{Cu} + 1)/3k_B$. Least-squares fitting of the experimental data (with $\theta = 0$) gave J = +2.93(2) cm⁻¹, $g_{Cu} = 2.10(1)$ and $R = 3 \times 10^{-7}$ (1) and J = -0.54(2) cm⁻¹, $g_{Cu} = 2.11(2)$, and $R = 1.1 \times 10^{-5}$ (2), *R* being the agreement factor defined as $\sum [(\chi_M T)_{exp} - (\chi_M T)_{calcd}]^2 / \sum [(\chi_M T)_{exp}]^2$. The theoretical curves match very well the experimental data for 1 and 2. Alternatively, a good fit of the experimental data for 2 in the 100 – 2.0 K range was obtained assuming that J = 0 with $g_{Cu} = 2.12(2)$, $\theta = -0.22(1)$ K [that is, zj = -0.61(1) cm⁻¹] and $R = 1.4 \times 10^{-5}$ (see solid line in Fig. S13).

9. Computational details and discussion

Density functional (DF) calculations were carried out on the actual crystal structures of **1** and **2** with the hybrid B3LYP method⁸ combined with the "broken-symmetry" approach,^{9,10} as implemented in the Gaussian 09 program¹¹. The triple- and double- ζ quality basis sets proposed by Ahlrichs and co-workers^{12,13} were used for the metal and non-metal atoms, respectively.

Density functional theory (DFT) calculations on the structures of 1 and 2 were performed in order to substantiate the magnitude of the ferromagnetic coupling in 1 and, more importantly, to give a clear-cut answer about the intra- or intermolecular nature of the antiferromagnetic coupling in 2. Hence, these calculations showed a triplet (S = 1) ground state fairly well separated from the singlet (S = 0) excited state for 1, whereas they evidenced almost degenerated triplet (S = 1) and singlet (S = 0) states for 2. The calculated values of the singlet-triplet energy gap ($\Delta E_{ST} = E_S - E_T = J$) are +3.382 (1) and +0.015 cm⁻¹ (2). The calculated J value for 1 agrees very well with the experimental value ($J = +2.93 \text{ cm}^{-1}$). The weak ferromagnetic coupling between the two Cu^{II} ions through the double oxo(carboxylate) bridge is as expected from the out-ofplane exchange pathway involved. In this case, the $d(x^2-y^2)$ -type orbitals containing the unpaired electron at each Cu^{II} ion ("magnetic orbitals") are parallel and they are connected in an equatorial-axial way through the double oxo(carboxylate) bridge. Depending on the value of the angle at the bridgehead oxo $[Cu(1)O(4)Cu(1)^i = 102.72(10)^\circ;$ symmetry code: (i) = -x+1, -y, -z], the accidental orthogonality between the magnetic orbitals can be achieved leading thus to a net ferromagnetic interaction¹⁴. On the other hand, the calculated J value for 2 is very small, if not negligible, strongly supporting the intermolecular nature of the antiferromagnetic coupling found. The π -orbital exchange pathway between the unpaired electrons of the Cu^{II} ions within the dinuclear metallacyclic entity is interrupted by the multiatom non-conjugated character of the 2,2'ethylenediphenylene diamidate bridges, the central ethylene group precluding the transmission of any intramolecular magnetic interaction.

10. Supplementary references

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