Three Individually Addressable Spin Qubits in a Single Molecule

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SUPPORTING INFORMATION



Scheme S1. Designed structure of the assembly of L^{4-} with a stoichiometric mixture of Ni(II) -grey- and Cu(II) -black- ions.

Experimental Procedures

Synthesis



Scheme S2. Synthesis of 1-methoxy-2,5-*bis*-(3-oxo-3-(2-hydroxyphenyl)-propanoyl)-benzene, H₄L.

Solvents and reagents employed in preparation of ligands and compounds were used as received from commercial suppliers. An exception was only made for Claisen condensations, where anhydrous THF (PureSolv Micro Solvent Purification Systems) was used as solvent to avoid any hydrolysis as possible side reaction. The intermediate 2,5-dimethyl anisole was converted to the corresponding carboxylic diacid following a reported procedures.¹

Dimethyl 2-methoxy-1,4-benzenedicarboxylate. 2-methoxy-1.4benzendicarboxylic acid (3.00 g, 0.015 mol) was suspended in 120 mL of MeOH, followed by dropwise addition of thionyl chloride (2.50 mL, 0.035 mol). After several minutes of stirring, the initial suspension turned into a solution that was then refluxed overnight (12 h). It was subsequently allowed to reach room temperature and the solvent was then removed under reduced pressure. The white solid obtained was dissolved in chloroform and a saturated aqueous solution of Na₂CO₃ was then added dropwise (until reaching pH 10) to remove the traces of unreacted diacid and the HCl formed. After 30 min of vigorous stirring, the mixture was transferred to a separation funnel. The organic layer was isolated, dried over Na₂SO₄ and filtered. After removal of the solvent under reduced pressure colorless crystals were isolated (av. Yield; 2.95 g, 86 %). ¹NMR (400 MHz, CDCl₃), δ(ppm): 3.91 (s, 3H, -OCH₃), 3.94 (s, 3H, -COOCH₃), 3.96 (s, 3H,-COOCH₃), 7.63-7.65 (m, 2H,-Ar-H), 7.80 (s, 1H, -Ar-H). IR (KBr pellet) v/cm⁻¹: 2958 s, 2934 b, 1702 s, 1613 s, 1574 s, 1492 s, 1464 s, 1449 s, 1436 s, 1401 s, 1284 s, 1258 s, 1226 s, 1194 s, 1121 s, 1085 s, 1029 s, 982 s, 961 s, 891 s, 873 s, 821 s, 787 s, 749 s, 683 s, 693 s.

1-methoxy-2,5-bis-(3-oxo-3-(2-hydroxyphenyl)-propanoyl)-benzene, H₄L. A 60% toluene dispersion of sodium hydride (2.36 g, 59.0 mmol) was suspended under nitrogen in 80 mL of hexanes. The mixture was stirred for 10 min. and the solvent was extracted with filter cannula. The procedure was repeated once again and dry THF (100 mL) was then added to the resulting white solid. In a separate Schlenk flask, 2-hydroxyacetophenone (3.65 g, 26.8 mmol) was dissolved under nitrogen in 30 mL of dry THF and added dropwise to the above suspension. This caused a yellow-green coloration of the reaction mixture and evolution of hydrogen. When the addition was complete, the mixture was stirred for 15 min at subsequently, room temperature and dimethyl 2-methoxy-1,4benzenedicarboxylate (3.00 g, 13.4 mmol) in THF (70 mL) was added. The reaction was then brought to reflux and maintained like this overnight. After 14h, the orange suspension was allowed to reach room temperature and the THF was removed under reduced pressure. The resulting orange solid was then suspended in water and acidified with 12% aqueous HCl to reach pH=3. A yellow precipitated was collected by filtration and purified by recrystallisation from acetone (av. Yield; 3.40 g, 59%). Single crystals of H₄L were obtained by dissolving the solid in boiling DMF and slowly cooling down the solution. ¹H NMR (400 MHz, CDCl₃), δ(ppm): 4.11 (s, 3H, -OCH₃), 4.66 and 4.68 (s, 0.5H,-

¹ Hannah, D. T. B.; Sherrington, D. C., *J. Mater. Chem.* **1997**, *7*, 1985-1991.

COCH₂CO), 6.90 (s, 1H, -COCHCOH), 6.95 (t, 2H, -Ar-H), 7.02 (t, 2H, -Ar-H), 7.35 (s, 1H, -COCHCOH), 7.49 (dd, 2H, -Ar-H), 7.60 (d+s, 2H, -Ar-H), 7.78 (dd, 2H, -Ar-H), 8.09 (d, 1H, Ar-H), 12.00 (s, 1H, Ar-OH), 12.11 (s, 1H, Ar-OH), 15.48 (s, 0.75H, -OHenol), 15.50 (s, 0.75H, -OHenol). ESI MS: m/z [H₃L]⁻ = 431.12. IR (KBr pellet) v/cm⁻¹: 3410 b, 3068 b, 1623 w, 1570 s, 1544 s, 1484 s, 1440 w, 1421 w, 1335 s, 1310 s, 1280 s, 1241 s, 1192 s, 1155 s, 1114 s, 1094 w, 1081 s, 1047 s, 1030 s, 906 s, 884 s, 864 s, 841 s, 814 s, 808 s, 767 s, 748 s, 729 s, 696 s, 620 s, 563 s, 524 s, 487 s, 429 s. EA (%); Calc. (Found for C₂₅H₂₀O₇·0.05DMF): C 69.27 (69.45), H 4.70 (4.98), N 0.16 (0.10).

[Ni₃Cu₃(L)₃(py)₉] (1). Tetrabutylammonium hydroxide (115 µL, 0.115 mmol) was added to a yellow-green solution of H₄L (12.0 mg, 0.028 mmol) in pyridine (8 mL) causing its immediate color change to orange. The mixture was stirred for 10 min and then it was added dropwise to a pyridine solution (8 mL) of $Cu(CIO_4)_2 \cdot 6H_2O$ (10.3 mg, 0.028 mmol) and Ni(ClO₄)₂·6H₂O (10.2 mg, 0.028 mmol), changing its appearance from blurry violet to clear yellow-brown. The resulting solution was covered and stirred at room temperature for 90 min before filtration. Depending on the humidity of the pyridine used, variable amounts of gelatinous precipitate (0-5 mg) were observed, while precipitate-free reaction mixtures were obtained when the solvent was completely dry (stored over molecular sieves). The filtrate was layered with hexanes to produce orange-brown blocks by liquid-liquid diffusion over a period of one month (average yield 10.5-14.2 mg, 48-65 %). IR (KBr pellet) v/cm-1: 3300 vb, 2927 w, 1597 s, 1547 s, 1498 vs, 1485 vs, 1438 vs, 1426 vs, 1375 s, 1351 w, 1321 s, 1246 s, 1195 s, 1135 w, 1095 w, 1068 w, 1023 s, 953 w, 937 w, 898 w, 848 s, 795 s, 745 vs, 695 vs. EA (%); Calc. (Found for 1.5.55H₂O): C 58.50 (58.25), H 4.26 (4.00), N 5.12 (4.88).

 $3 H_4L + 3 Ni(CIO_4)_2 + 3 Cu(CIO_4)_2 + 12 Bu_4NOH + 9 py \rightarrow$ $\rightarrow [Ni_3Cu_3(L)_3(py)_9] + 12 Bu_4NCIO_4 + 12 H_2O (eq. S1)$

X-ray crystallography

Crystallographic data for ligand H₄L and compound **1** were collected at 100 K using a Bruker D8 diffractometer with a PHOTON 100 detector at the Advanced Light Source beamline 11.3.1 of Lawrence Berkeley National Laboratory, from a silicon 111 monochromator ($\lambda = 0.7749$ Å). Data reduction and absorption corrections in both cases were performed with SAINT and SADABS respectively.² The structures were solved by intrinsic phasing with SHELXT³ and refined by full-matrix least-squares on *F*² with SHELXL.⁴ Non-hydrogen atoms were refined anisotropically while hydrogen atoms were placed geometrically on their carrier atom and refined using a suitable riding model. Exceptionally, hydrogen atoms of phenol and enol moieties in the structure of H₄L were found in a difference Fourier

² G. M. Sheldrick, 2012, *SAINT* and *SADABS*, Bruker AXS Inc., Madison, Wisconsin, USA.

³ G. M. Sheldrick, Acta Cryst. A 2015, 71, 3-8.

⁴ G. M. Sheldrick, Acta Cryst. C 2015, 71, 3-8.

map (resolution 0.71 Å) and refined freely with their thermal parameter 1.5 times that of their carrier oxygen atom.

In the structure of compound 1, one of the pyridine molecules coordinated to Ni3 was refined as disordered over two positions (N8/N18) with relative occupancies of 0.44:0.56 using a rigid body restraint (AFIX 66) and displacement parameters restraints. The three methoxy substituents O4-C16, O11-C41 and O18-C66 showed some disorder and were refined with displacement parameters restraints as well as with a distance restraint (O-C). Refinement of a disorder was attempted for one of the methoxy groups (O4–C16) since a residual density peak (3 e⁻/Å³) was found in the vicinity of the C14–H14A bond. The model with two possible positions of the –OMe group to the phenyl ring (O4–C16 and O4–C14) did not converge and was therefore discarded. Three lattice pyridine molecules (N1S, N2S and N3S) were refined with rigid body and displacement parameters restraints due to disorder. A large number of weak residual electron density peaks remained in the lattice that seemed to form additional highly disordered/diffuse lattice pyridine molecules. Their refinement did not converge properly, and PLATON/SQUEEZE was used to analyze and take into account the corresponding void spaces. A total of 677 electrons were thus recovered over three voids of 185, 1500 and 283 Å³. These figures would agree with at most 9 diffuse lattice pyridine molecules per unit cell, so that 4 pyridine per formula unit were added to the formula content.

All crystallographic details can be found in CCDC 2168791-2168792 (for H₄L and **1**, respectively). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Physical Measurements

Variable-temperature magnetic susceptibility data were obtained with a Quantum Design MPMS5 SQUID magnetometer at the "Unitat de Mesures Magnètiques" of the Universitat de Barcelona. Pascal's constants were used to estimate diamagnetic corrections to the molar paramagnetic susceptibility and a correction was applied for the sample holder.

X-Band EPR spectra (9.42 GHz) of powdered samples were collected on a Bruker ESP300E spectrometer with a liquid helium cryostat. Pulsed Q-band measurements were performed with a custom-built spectrometer.⁵ The pulse sequences used were $\pi/2-\tau-\pi-\tau$ -echo (Hahn echo) for determination of echo-detected EPR spectra and phase memory time and $\pi-T-\pi/2-\tau_{fix}-\pi-\tau_{fix}$ -echo (inversion recovery) for determination of spin–lattice relaxation time.

IR spectra were recorded as KBr pellets, in the range 4000–400 cm⁻¹, with a Nicolet 5700 FT-IR spectrometer.

Elemental analyses were performed at Scientific and Technological Centers of the University of Barcelona using an elemental organic analyzer Thermo EA Flash 2000 working in standard conditions recommended by the supplier of the instrument (helium flow 140 ml/min, combustion furnace at 950°C, chromatografic column oven at 65°C). Mass spectra of the compounds were obtained using the MALDI-TOF technique, while ligands were analyzed using the ESI technique. Molecular ions were studied in both positive and negative mode on the THF

⁵ Tkach, I.; Baldansuren, A.; Kalabukhova, E.; Lukin, S.; Sitnikov, A.; Tsvir, A.; Ischenko, M.; Rosentzweig, Y.; Roduner, E., *Appl. Magn. Reson.* **2008**, *35*, 95-112

solutions of ligands and compounds. MALDI-TOF spectrograms were collected in the reflector mode on the 4800 *Plus* MALDI TOF/TOF (ABSciex-2010) instrument equipped with Nd:YAG solid state laser (355 nm, frequency 200 Hz, pulse 3-7 ns). Analyses were carried out on the solution of the compound mixed with the matrix containing dichloromethane solution of DCTB (10 mg/mL; *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile (1:1 volume ratio spotted on the sample plate and left to dry before the analysis by MALDI-TOF). ESI mass spectrograms were determined using a LC/MSD-TOF (Agilent Technologies) with a dual source equipped with a lock spray for internal reference introduction.

Computational details

Kohn-Sham density functional theory (DFT) calculations were performed using the PBE0 functional⁶ with the Gaussian 16.A03 software.⁷ C, H, N and O atoms were described with the SVP basis sets⁸ while Cu and Ni atoms were described with LANL2DZ basis sets and related effective core potentials.⁹ Default convergence thresholds were used in the geometry optimizations.

⁶ Adamo, C.; Barone, V. *J. Chem. Phys.* **1999**, *110*, 6158–6170.

⁷ M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.

⁸ A. Schaefer, H. Horn, and R. Ahlrichs, J. Chem. Phys., **1992**, 97, 2571-77.

⁹ P. J. Hay and W. R. Wadt, *J. Chem. Phys.*, **1985**, *82*, 270-83

	H ₄ L	1
Formula	$C_{25}H_{20}O_7$	$C_{155}H_{128}N_{16}O_{21}Cu_{3}Ni_{3}$
Mr	432.41	2917.47
Crystal system	Orthorhombic	Triclinic
Space group	Fdd2	<i>P</i> -1
<i>a</i> (Å)	22.347(8)	17.429(5)
b (Å)	67.02(2)	22.792(7)
<i>c</i> (Å)	5.194(2)	23.211(6)
α (°)	90	119.151(4)
β (°)	90	92.989(4)
γ (°)	90	108.934(4)
V (Å ³)	7779(5)	7366(4)
Ζ	16	2
$ ho_{calc}$ (g/cm ³)	1.477	1.316
µ (cm ⁻¹)	0.131	1.220
Shape and colour	Yellow plate	Orange block
Crystal size (mm ³)	0.170x0.050x0.020	0.080x0.040x0.040
λ (Å)	0.7749	0.7749
Т (К)	100(2)	100(2)
Reflections (Rint)	4437 (0.0395)	27132 (0.0608)
Parameters	302	1562
Restraints	1	494
R ₁ (all data) ^a	0.0484	0.1190
R₁ [<i>l>2σ(l)</i>]ª	0.0389	0.0795
wR ₂ (all data) ^b	0.0938	0.2459
wR ₂ [/>2 <i>σ(l)</i>] ^b	0.0891	0.2140
S (all data) ^c	1.042	1.064
S [<i>I>2σ(I)</i>]°	1.042	1.056
Largest res. (e ų)	0.244/-0.216	3.459/–1.169

Table S1: Crystallographic data H₄L and compound **1**.

^a R₁ = $\Sigma ||F_o| - |F_c|| / \Sigma |F_o|$ ^b wR₂ = { $\Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2]$ }^{1/2} w = 1 / [$\sigma(F_o^2) + (aP)^2 + bP$] where P is [$2F_c^2 + Max(F_o^2, 0)$] / 3 ^c S = { $\Sigma [w(F_o^2 - F_c^2)^2] / (n - p)$ }^{1/2}

$\begin{array}{cccccccccccccccccccccccccccccccccccc$								
C1-C2 1.394(4) C8-C9 1.370(3) C12-C11 1.388(3) C21-C22 1.378(3) C2-C3 1.373(4) C9-O3 1.336(3) C11-C10 1.408(3) C22-C23 1.396(3) C3-C4 1.400(4) C9-C10 1.478(3) C13-C17 1.484(3) C23-C24 1.379(3) C4-C5 1.374(4) C10-C15 1.416(3) C17-O5 1.327(3) C24-C25 1.392(3) C5-C6 1.408(4) C15-O4 1.356(3) C17-C18 1.364(3) C25-C20 1.417(3) C6-C1 1.418(3) O4-C16 1.436(3) C18-C19 1.440(3) C25-O7 1.349(3) C6-C7 1.479(3) C15-C14 1.391(2) C19-O6 1.271(3) C14-C13 1.393(3) C19-C20 1.469(3)	01–C1	1.351(3)	C7–C8	1.433(3)	C13–C12	1.391(3)	C20–C21	1.407(3)
C2-C3 1.373(4) C9-O3 1.336(3) C11-C10 1.408(3) C22-C23 1.396(3) C3-C4 1.400(4) C9-C10 1.478(3) C13-C17 1.484(3) C23-C24 1.379(3) C4-C5 1.374(4) C10-C15 1.416(3) C17-O5 1.327(3) C24-C25 1.392(3) C5-C6 1.408(4) C15-O4 1.356(3) C17-C18 1.364(3) C25-C20 1.417(3) C6-C1 1.418(3) O4-C16 1.436(3) C18-C19 1.440(3) C25-O7 1.349(3) C6-C7 1.479(3) C15-C14 1.391(2) C19-O6 1.271(3) C14-C13 1.393(3) C19-C20 1.469(3)	C1–C2	1.394(4)	C8–C9	1.370(3)	C12–C11	1.388(3)	C21–C22	1.378(3)
C3-C4 1.400(4) C9-C10 1.478(3) C13-C17 1.484(3) C23-C24 1.379(3) C4-C5 1.374(4) C10-C15 1.416(3) C17-O5 1.327(3) C24-C25 1.392(3) C5-C6 1.408(4) C15-O4 1.356(3) C17-C18 1.364(3) C25-C20 1.417(3) C6-C1 1.418(3) O4-C16 1.436(3) C18-C19 1.440(3) C25-O7 1.349(3) C6-C7 1.479(3) C15-C14 1.391(2) C19-O6 1.271(3) C14-C13 1.393(3) C19-C20 1.469(3)	C2–C3	1.373(4)	C9–O3	1.336(3)	C11–C10	1.408(3)	C22–C23	1.396(3)
C4-C5 1.374(4) C10-C15 1.416(3) C17-O5 1.327(3) C24-C25 1.392(3) C5-C6 1.408(4) C15-O4 1.356(3) C17-C18 1.364(3) C25-C20 1.417(3) C6-C1 1.418(3) O4-C16 1.436(3) C18-C19 1.440(3) C25-O7 1.349(3) C6-C7 1.479(3) C15-C14 1.391(2) C19-O6 1.271(3) C7-O2 1.274(3) C14-C13 1.393(3) C19-C20 1.469(3)	C3–C4	1.400(4)	C9–C10	1.478(3)	C13–C17	1.484(3)	C23–C24	1.379(3)
C5-C6 1.408(4) C15-O4 1.356(3) C17-C18 1.364(3) C25-C20 1.417(3) C6-C1 1.418(3) O4-C16 1.436(3) C18-C19 1.440(3) C25-O7 1.349(3) C6-C7 1.479(3) C15-C14 1.391(2) C19-O6 1.271(3) C7-O2 1.274(3) C14-C13 1.393(3) C19-C20 1.469(3)	C4–C5	1.374(4)	C10–C15	1.416(3)	C17–O5	1.327(3)	C24–C25	1.392(3)
C6-C1 1.418(3) O4-C16 1.436(3) C18-C19 1.440(3) C25-O7 1.349(3) C6-C7 1.479(3) C15-C14 1.391(2) C19-O6 1.271(3) C7-O2 1.274(3) C14-C13 1.393(3) C19-C20 1.469(3)	C5–C6	1.408(4)	C15–O4	1.356(3)	C17–C18	1.364(3)	C25–C20	1.417(3)
C6-C71.479(3)C15-C141.391(2)C19-O61.271(3)C7-O21.274(3)C14-C131.393(3)C19-C201.469(3)	C6–C1	1.418(3)	O4–C16	1.436(3)	C18–C19	1.440(3)	C25–O7	1.349(3)
C7–O2 1.274(3) C14–C13 1.393(3) C19–C20 1.469(3)	C6–C7	1.479(3)	C15–C14	1.391(2)	C19–O6	1.271(3)		
	C7–O2	1.274(3)	C14–C13	1.393(3)	C19–C20	1.469(3)		

Table S2. Bond distances [Å] within the molecule of H₄L.

Table S3. Hydrogen bonding and $\pi \cdots \pi$ contacts within the lattice of H₄L.

D–H…A	D–H (Å)	H…A (Å)	D–A (Å)	D–H…A (⁰)
01–H1…O2	0.88(3)	1.77(3)	2.567(2)	149(3)
O3–H3…O2	0.97(3)	1.64(3)	2.518(2)	149(3)
C8–H8A…O4	0.95	2.13	2.791(3)	125.2
O5–H5…O6	0.91(3)	1.66(3)	2.494(2)	152(3)
O7–H7…O6	0.86(3)	1.80(3)	2.572(2)	147(3)
O1#–H1#…O5	0.88(3)	2.43(4)	3.065(3)	129(3)
O7–H7…O3#	0.86(3)	2.54(3)	3.181(3)	132(3)
C24#1–H24A#1…O7	0.95	2.54	3.284(3)	135.6

$\pi \cdots \pi$		

C…C	d (Å)	С…С	d (Å)
phenol-β-diketone (O1···C17#2)	3.206(3)	β-diketone-β-diketone (C7…O6#2; O2…C19#2)	3.111(3) 3.104(3)

Symmetry operation: # = 1/2+x, y, 1/2+z; #1 = 3/2-x, 1-y, 1/2+z; #2 = -1/2+x, y, 1/2+z

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Ni1–Cu1	3.032(1)	Ni3–N9	2.166(7)	N5–Ni2–O16	92.0(2)
Ni2–Cu2	3.054(1)	Ni3–O12	1.976(4)	N5–Ni2–O5	88.6(2)
Ni3–Cu3	3.041(1)	Ni3–O13	2.025(4)	N5–Ni2–O17	88.7(2)
Ni1…Ni2	10.226(2)	Ni3–O19	1.977(4)	N6–Ni2–O16	92.8(2)
Ni2…Ni3	10.157(2)	Ni3-020	1.998(3)	N6-Ni2-O6	91.7(2)
Ni3…Ni1	10.325(3)	N1–Cu1–O8	103.0(2)	N6-Ni2-O5	87.0(2)
Ni1–N3	2.136(5)	N1–Cu1–O1	103.8(2)	N6-Ni2-017	89.5(2)
Ni1–N2	2.086(5)	N1–Cu1–O2	94.6(2)	017–Ni2–O16	91.0(2)
Ni1–O10	1.981(4)	N1–Cu1–O9	95.6(2)	016–Ni2–O6	79.1(2)
Ni1–O3	1.962(3)	O8–Cu1–O1	91.7(2)	06–Ni2–O5	91.5(2)
Ni1-02	2.022(4)	O1–Cu1–O2	89.7(1)	O5–Ni2–O17	98.3(2)
Ni1–O9	2.009(4)	O2–Cu1–O9	81.9(2)	N7–Cu3–O21	106.4(2)
Cu1–O9	1.973(4)	O9–Cu1–O8	90.5(2)	N7-Cu3-O14	100.8(2)
Cu1–O2	1.988(3)	N3-Ni1-O9	93.0(2)	N7-Cu3-O20	95.8(2)
Cu1–O1	1.885(4)	N3-Ni1-O2	89.7(2)	N7-Cu3-O13	93.8(2)
Cu1–O8	1.884(4)	N3–Ni1–O10	88.6(2)	O21–Cu3–O14	93.0(2)
Cu1–N1	2.195(6)	N3-Ni1-O3	87.2(2)	O21–Cu3–O20	89.7(2)
Ni2-016	2.013(5)	N2-Ni1-O2	92.0(2)	O20-Cu3-O13	81.0(2)
Ni2-06	2.003(4)	N2-Ni1-O9	92.8(2)	O13–Cu3–O14	90.1(2)
Ni205	1.966(4)	N2-Ni1-O10	90.5(2)	N8-Ni3-O20	88.3(4)
Ni2-017	1.970(4)	N2-Ni1-O3	87.1(2)	N8–Ni3–O13	89.3(4)
Ni2–N5	2.130(6)	O3-Ni1-O2	91.1(2)	N8–Ni3–O19	92.6(4)
Ni2–N6	2.136(6)	O2-Ni1-O9	80.2(2)	N8–Ni3–O12	92.3(4)
Cu2–O16	1.983(3)	O9–Ni1–O10	91.5(2)	N9–Ni3–O13	89.7(2)
Cu2-06	1.982(5)	O10-Ni1-O3	97.3(2)	N9-Ni3-O20	92.6(2)
Cu2–O15	1.908(4)	N4–Cu2–O7	97.8(2)	N9–Ni3–O19	88.6(2)
Cu2–N4	2.219(6)	N4–Cu2–O15	99.1(2)	N9–Ni3–O12	86.6(2)
Cu2–07	1.910(4)	N4–Cu2–O6	96.6(2)	012–Ni3–013	90.8(1)
Cu3–N7	2.239(7)	N4–Cu2–O16	102.1(2)	013–Ni3–O20	80.2(2)
Cu3–O13	2.018(4)	O15–Cu2–O7	96.1(2)	O20-Ni3-O19	91.8(2)
Cu3–O20	1.970(4)	07–Cu2–O6	88.9(2)	019–Ni3–O12	97.1(2)
Cu3–O21	1.891(4)	O6–Cu2–O16	80.3(2)	Ni2…Ni1…Ni3	59.24(1)
Cu3–O14	1.889(4)	O16–Cu2–O15	89.2(2)	Ni1…Ni3…Ni2	59.90(1)
Ni3–N8	2.225(9)	N5-Ni2-O6	90.9(2)	Ni3…Ni2…Ni1	60.87(1)

Table S4. Interatomic distances [Å] and angles [°] for compound 1.

$R_0(Cu^{\parallel})$	B(Cu ^{ll})	Bond	Ri	V(Cu ^{ll})	Bond	Ri	V(Cu ^{ll})	Bond	Ri	V(Cu ^{ll})
/(ou)	D(04)	Dona	7.4	v(ou)	Dona	7.4	v(ou)	Bond	, (v(ou)
1.649	0.37	Cu1–O9	1.973	0.417	Cu2–O16	1.983	0.405	Cu3–O13	2.017	0.370
1.649	0.37	Cu1–O1	1.885	0.528	Cu2–O6	1.982	0.407	Cu3–O14	1.889	0.523
1.649	0.37	Cu1–O2	1.987	0.401	Cu2–O15	1.908	0.497	Cu3–O20	1.970	0.420
1.649	0.37	Cu1–O8	1.884	0.530	Cu2–O7	1.909	0.495	Cu3–O21	1.891	0.520
1.713	0.37	Cu1–N1	2.194	0.273	Cu2–N4	2.219	0.255	Cu3–N7	2.239	0.241
BVS				2.149			2.059			2.074

Table S5: BVS analysis for compound 1.

<i>R</i> ₀(Ni ^{II})	B(Ni ^{II})	Bond	Ri	V(Ni ^{II})	Bond	Ri	V(Ni ^Ⅱ)	Bond	Ri	V(Ni [∥])
1.670	0.37	Ni1-09	2.009	0.400	Ni2-05	1.966	0.449	Ni3-012	1.976	0.437
1.670	0.37	Ni1-010	1.981	0.431	Ni2-06	2.002	0.408	Ni3–O13	2.025	0.383
1.670	0.37	Ni1-02	2.022	0.386	Ni2–O16	2.013	0.396	Ni3–O19	1.978	0.435
1.670	0.37	Ni1-03	1.962	0.454	Ni2-017	1.970	0.444	Ni3020	1.998	0.412
1.647	0.37	Ni1–N2	2.086	0.305	Ni2–N5	2.130	0.271	Ni3–N8	2.23	0.207
1.647	0.37	Ni1–N3	2.136	0.266	Ni2–N6	2.136	0.267	Ni3–N9	2.164	0.247
BVS				2.242			2.235			2.121



Figure S1. ESI mass spectrogram of ligand H₄L in THF solution, in the negative mode. *Inset*: Experimental and theoretical isotopic distribution of the most abundant molecular peak.



Figure S2. ¹H NMR spectrum of ligand H₄L in CDCl₃.



Figure S3. Representation of ligand H₄L emphasizing the four triangular hydrogen bonds that it forms in the solid state with each of two neighboring molecules located laterally at opposite sides. C, O and H are grey, red and white respectively.



Figure S4. Representation of ligand H₄L emphasizing stacking of ribbons forming thick sheets that stand next to each other. The parallel planes that contain the ribbons in one sheet are approximately perpendicular to the planes in the adjacent sheet.



Figure S5. *Top*: MALDI(+) mass spectrogram of $[Ni_3Cu_3(L)_3(py)_9]$ (1) in THF solution in the DCTB matrix (1:1). *Bottom*: Isotopic distribution of the main molecular peak, $[(CuNi)(L)]_3^+$. The slight offset between the expected and the observed signal is within the experimental error of the technique ($\Delta m/z < 0.1$).



Figure S6. Comparison between the isotopic distribution of the main observed molecular peak of **1** from the MALDI-TOF data (black lines) and simulated isotopic pattern for any possible $[Ni_xCu_y(L)_3]^+$ ion (x = 0 to 6, y = 6 - x; red lines).



Figure S7. Labelled representation of [Ni₃Cu₃(L)₃(py)₉] (**1**). Grey atoms are C and H atoms are not shown.



Figure S8. Representation of various molecules of **1** along the crystallographic *c* axis, emphasizing the stacks of sheets formed by these approximately parallel to the idealized molecular plane, and interacting mutually by interdigitation of their axial pyridine ligands.



Figure S9. Representation of one sheet of molecules of **1** perpendicular to the crystallographic c axis, emphasizing the six neighboring molecules surrounding each of them.

Simulation of the variable temperature magnetic susceptibility data

The spin Hamiltonian describing the magnetic properties of **1** is as follows:

$$\widehat{H} = \mu_B B \sum_{i} g_i \widehat{S}_i - 2J_{Cu-Ni} \left(\widehat{S}_{Cu(1)} \widehat{S}_{Ni(1)} + \widehat{S}_{Cu(2)} \widehat{S}_{Ni(2)} + \widehat{S}_{Cu(3)} \widehat{S}_{Ni(3)} \right)$$

in which \hat{S}_i is $\hat{S}_{Cu(i)}$ or $\hat{S}_{Ni(i)}$, with values $\frac{1}{2}$ and 1, respectively, g_i is $g_{Cu(i)}$ or $g_{Ni(i)}$ (*i* = 1 to 3). The strong correlation between analogous parameters in each NiCu pair however forces to impose the equivalence of 1 to 3. Considering an additional term \hat{H}_{zJ} to take into account inter-NiCu pair weak interactions treated in the mean-field approximation,¹⁰ the Hamiltonian becomes:

$$\widehat{H} = 3 \times \{ \mu_B B [g_{Cu} \hat{S}_{Cu} + g_{Ni} \hat{S}_{Ni} - 2 J_{Cu-Ni} (\hat{S}_{Cu} \hat{S}_{Ni})] - \widehat{H}_{zJ'} \}$$

The expression of the magnetic susceptibility then reduces to three times the one derived for a related [NiCu] complex,¹¹ which was therefore used.

¹⁰ C. J. O'Connor, *Prog. Inorg. Chem.* 1982, **29**, 203-283.

¹¹ I. Morgenstern-Badarau, M. Rerat, O. Kahn, J. Jaud and J. Galy, *Inorg. Chem.* 1982, **21**, 3050-3059

On the presence and strength of interaction among NiCu pairs

The most likely mode of magnetic coupling among the NiCu pairs in **1** is throughspace and therefore dipolar. The dipolar interaction J_D can be estimated using a point dipole approximation on basis of the distances in the structure. We note however that this is a very crude model in the present case, since the spin density of the ground S=1/2 state of each NiCu pair is necessarily delocalized over the Ni(μ -O)₂Cu moiety. Considering the separation between the centroids of these moieties in the structure of **1** (ca. 12.81-12.91 Å) gives a J_D/k_B of ca. 1.15 mK (i.e. $J_D = 0.8 \times 10^{-3}$ cm⁻¹). Considering the shortest separation between the spin densities through the Ni…Ni separations (ca. 10.16-10.32 Å) gives a J_D/k_B of ca. 2.3 mK (i.e. $J_D = 1.6 \times 10^{-3}$ cm⁻¹). These values (likely over-estimated) are two orders of magnitude smaller than the value of zJ'. Even though there could be some exchange coupling at work, this means that the mean-field term zJ' is likely strongly over-estimating the interaction among the NiCu pairs, probably because the decrease of χT at the lowest temperatures is at least in part due to magnetic anisotropy arising from the Ni(II) single-ion anisotropy.

Such small interaction is in agreement with EPR observations, basically that at the temperatures used (15 K on the solid, 3.2-4.2 K on the frozen solution) there is no sign of the effect of interactions.

Examples of the effect of very weak (similar to here) and weak coupling (ca. one order of magnitude larger) among spin ½ systems can be found in dinuclear V(IV) complexes reported by Sessoli et al.¹² and some of us.¹³ While the spectrum of the latter is characteristic of a weakly-interacting system with a complex set of lines likely resulting from the combination of splitting processes caused by both hyperfine spin-nuclei and spin–spin interactions, in the former, the observation of splitting is questionable even with the well-resolved narrow lines of the vanadyl ions. It is therefore normal that with similar or even weaker coupling here, there is no sign of the effect of the coupling in our EPR spectra. The effect of such very weak interactions could only be noticed with very narrow line broadening, i.e. in measurements done on (diluted) single crystals, and ideally at very low temperatures.

¹² M. Atzori, A. Chiesa, E. Morra, M. Chiesa, L. Sorace, S. Carretta and R. Sessoli, *Chem. Sci.* 2018, **9**, 6183-6192

¹³ I. Borilovic, P. J. Alonso, O. Roubeau and G. Aromí, *Chem. Commun.* 2020, **56**, 3139-3142

Simulation of pulsed-EPR Hahn-echo and inversion recovery data

The inversion recovery data at 3.2 K show the presence of a clear much faster decay at initial times. This is commonly observed and is typically ascribed to a faster relaxation occurring through spin diffusion. The data were therefore reproduced with a bi-exponential decay model according to the following equation (1):

$$I = A_{SD} exp\left(\frac{-t_d}{T_1^{SD}}\right) + Aexp\left(\frac{-t_d}{T_1}\right) \qquad (1)$$

Simulation of the Hahn echo decay at 3.2 K was initially done with a single exponential decay model (equation 2 below), but the relatively poor agreement indicated the likely presence of more than one relaxation time. Simulation with both bi-exponential (equation 3 below) and stretched exponential (equation 4 below) decays were therefore also attempted. The simulations are shown in Figure S10.

$$I = Aexp\left(\frac{-2\tau}{T_M}\right) \quad (2)$$

$$I = A_s exp\left(\frac{-2\tau}{T_{M,s}}\right) + A_f exp\left(\frac{-2\tau}{T_{M,f}}\right) \quad (3)$$

$$I = Aexp\left(\frac{-2\tau}{\beta T'_M}\right)^{\beta} \quad (4)$$

Both bi-exponential and stretched exponential models provide a better simulation, with slightly better agreement parameters for the former (see Figure S10). The derived stretch parameter β inferior to 1 is indicative of a distribution of relaxation times, rather broad considering β is closer to 0.5 than 1. This is in agreement with the fact the data can be reproduced with two significantly different relaxation times. Considering that in such conditions the mean phase memory time T_M' does not clearly give the picture of very different relaxation times, we have preferred to report in the main text the results of the simulation with bi-exponential decay model.



Figure S10. Hahn-echo decay at T = 3.2 K and g = 2.207 for a dilute (*ca.* 1 mM) frozen solution of **1** in deuterated THF, with the best-simulation (full red lines) obtained with respectively bi-exponential (top), single exponential (middle) and stretched exponential (bottom) decay models.