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Click chemistry as a route to the synthesis of structurally new and magnetically interesting coordination clusters: A $\{Ni^{II}_8\}$ complex with a trapezoidal prismatic topology

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Experimental Section

Synthesis. All manipulations were performed under aerobic conditions using materials (reagent grade) and solvents as received, unless otherwise noted. ***Caution!*** Azide salts, and their corresponding metal complexes, are potentially explosive; such compounds should be synthesized and used in small quantities, and treated with utmost care at all times. Complex **1** was found to be safe when used in small quantities under the reported conditions.

***rac*-mpmH:** To a solution of 2-acetylpyridine (3.00 g, 24.8 mmol) in methanol (50 mL) at 0 °C was added $NaBH_4$ (0.94 g, 25 mmol) portionwise over 10 mins. The reaction was allowed to warm to room temperature and stirred for 12 h. The reaction was concentrated to ~25 mL and then the residual borohydride was quenched by the dropwise addition of water. Once the effervescence had ceased, a further 75 mL water was added and extracted with EtOAc (3 × 50 mL). The combined organic layers were washed with brine, dried (Na_2SO_4) and the solvent removed *in vacuo* to yield the title compound (2.77 g, 91% yield) as a pale-yellow oil. M.p.: 53-54 ^oC. ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm): 8.53 (1H, d, J = 4.72 Hz, H7), 7.68 (1H, td, J = 7.79, 6.39 Hz, H5), 7.29 (1H, d, J = 7.94 Hz, H4), 7.19 (1H, dd, J = 5.29, 5.14 Hz, H6), 4.89 (1H, q, J = 6.57 Hz, H2), 4.10 (1H, s, OH), 1.50 (3H, d, J = 6.59 Hz, H1); ^{13}C NMR ($CDCl_3$, 400 MHz) δ (ppm): 162.9 (C3), 147.9 (C7), 137.1 (C5), 122.3 (C4), 119.9 (C6), 68.8 (C2); IR (cm^{-1}): 3356, 2975, 1595, 1477, 1364, 1282, 1081, 1017, 904, 784, 751, 608, 538. Elemental analysis (%) calcd for C_7H_9NO: C 68.27, H 7.37, N 11.37; found C 68.25, H 7.47, N 11.52.

$[Ni_8(N_3)_8(mtz)_4(rac\text{-}mpm)_4(rac\text{-}mpmH)_4]$ (1): To a stirred, white suspension of *rac*-mpmH (0.025 g, 0.20 mmol) and NaN_3 (0.026 g, 0.40 mmol) in MeCN (15 mL) was added solid $Ni(ClO_4)_2{\cdot}6H_2O$ (0.073 g, 0.20 mmol). The resulting green solution was stirred for 40 min, filtered, and left for slow evaporation at room temperature. After a period of two months, X-ray quality turquoise plate-like crystals of **1**·$2.2H_2O$ were formed, and these were collected by filtration, washed with cold MeCN (2 × 2 mL) and dried in air. The yield was 30 %. The air-dried, crystalline material was analyzed as **1**·$2H_2O$. Elemental analysis

(%) calcd for **1**·2H_2O (MW = 2155.25 g mol^{-1}): C 35.67, H 3.93, N 31.19; found: C 35.59, H 3.86, N 31.32. Selected IR data (ATR): ν = 2057 (vs, ν(N-N)), 1653 (m), 1601 (m), 1527 (m), 1380 (m), 1286 (m), 1177 (w), 1083 (m), 1052 (m), 1021 (m), 967 (m), 761 (s), 701 (m), 699 (m), 530 (w), 472 (m), 435 (m).

Synthetic details. For the successful synthesis of crystalline material of complex **1** some helpful hints should be noted. The 1:1:2 molar ratio between $Ni(ClO_4)_2·6H_2O$, *rac*-mpmH and NaN_3 should be always kept constant for the clean and crystalline formation of **1**. Different ratios of the three reagents, i.e., 1:1:3, 1:2:2 and 2:1:2, still gave **1** but in much smaller yields and always contaminated with unreacted metal salts and/or NaN_3. Another important synthetic variable that should always be absent from this reaction is the external base. We noted that the addition of an external base, i.e. R_3N (R = Me, Et, etc), in the reaction that led to complex **1**, facilitated the rapid precipitation of amorphous green solids which could not be further characterized or crystallized.

Physical Measurements. Infrared spectra were recorded in the solid state on a Bruker's FT-IR spectrometer (ALPHA's Platinum ATR single reflection) in the 4000-400 cm^{-1} range. NMR spectra were obtained on a Bruker Avance DPX-400 MHz instrument and are referenced to the residual proton signal of the deuterated solvent for ^1H spectra, and to the carbon multiplet of the deuterated solvent for the ^{13}C spectra, according to published values. Melting points were recorded on a Kofler hot-stage apparatus. Elemental analyses (C, H, and N) were performed by Atlantic Microlab Inc. Magnetic susceptibility studies were performed at the University of Barcelona, Chemistry Department, on a MPMS5 Quantum Design susceptometer. Pascal's constants were used to estimate the diamagnetic correction, which was subtracted from the experimental susceptibility to give the molar paramagnetic susceptibility (χ_M).[S1] The magnetic data were fit to the appropriate spin Hamiltonian using the PHI software.[S2] Quality of the fits were parametrized as $R(\chi_M T) = (\chi_M T_{exp} - \chi_M T_{calc})^2/(\chi_M T_{exp})^2$ and $R(M) = (M_{exp} - M_{calc})^2/(M_{exp})^2$.

Single-crystal X-ray Crystallography. A turquoise plate-like crystal (0.120 × 0.120 × 0.050 mm^3) of **1**·2.2H_2O was mounted on a MiTeGen kapton loop in the 100(2) K nitrogen

cold stream provided by an Oxford Cryosystems Cryostream 700 Plus apparatus. The crystal was transferred to the goniometer head of a Bruker D8 diffractometer equipped with a PHOTON 100 detector on beamline 11.3.1 at the Advanced Light Source in Berkeley National Laboratory. Diffraction data were collected in synchrotron radiation, monochromated using silicon(111) to a wavelength of 0.7749 Å. A total of 40016 reflections were collected, of which 4362 were unique (R_{int} = 0.0335) and 3137 were observed [$I > 2\sigma(I)$]. The structure was solved by intrinsic phasing and refined by full-matrix least-squares on F^2 (SHELXL-2014/7)[S3] using 467 parameters and 695 restraints.

All fully occupied non-hydrogen atoms were refined anisotropically, except from the low occupancy disordered water molecules. Hydrogen atoms on the methyl groups were found in the difference map, while the remaining were placed as geometrically constrained and refined using a riding model. Hydrogen atoms could neither be found nor placed on the water molecules and one of the ligand oxygen atoms and therefore they were omitted from the refinement but not the chemical formula of the compound. Displacement and geometrical restraints were used to model the disorder of the ligands. The programs used for molecular graphics were MERCURY[S4] and DIAMOND.[S5] Unit cell parameters and structure solution and refinement data are listed in Table S1. Selected interatomic distances and angles are listed in Table S2. Crystallographic data for the structure reported in this work have been deposited to the Cambridge Crystallographic Data Centre (CCDC) as supplementary publication numbers: CCDC-1911866 (**1**). Copies of these data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 2EZ, UK; FAX: (+44) 1223 336033, or online via www.ccdc.cam.ac.uk/data_request/cif or by emailing data_request@ccdc.cam.ac.uk.

Table S1. Crystallographic data for complex **1**·2.2H_2O

Complex	**1**·2.2H_2O
Formula	$C_{64}H_{84.4}N_{48}Ni_8O_{10.2}$
FW / g mol^{-1}	2159.07
Crystal system	Orthorhombic
Space group	Fddd
a / Å	18.5858(8)

b / Å	24.9993(10)
c / Å	40.6220(17)
α / º	90
β / º	90
γ / º	90
V / Å^3	18874.3(14)
Z	8
T / K	100(2)
λ / Å	0.7749
Radiation type	synchrotron
θ range (°) for data collection	2.215 - 27.971
ρ_{calc} / g cm^{-3}	1.520
μ / mm^{-1}	2.065
F(000)	8880
Measd / independent (R_{int}) reflns	40016 / 4362 (0.0335)
Obsd reflns [$I > 2\sigma(I)$]	3137
R_1[a]	0.0950
wR_2[b]	0.2535
GOF on F^2	1.039
$(\Delta\rho)_{max,min}$ / e Å^{-3}	1.002, -0.839

[a] $R_1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$. [b] $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$, $w = 1/[\sigma^2(F_o^2) + [(ap)^2 + bp]$, where $p = [\max(F_o^2, 0) + 2F_c^2]/3$.

Table S2. Selected interatomic distances (Å) and angles (°) for complex **1**·2.2H_2O[a]

Bond lengths			
Ni1-N1	1.980(17)	Ni2-N2	1.99(2)
Ni1-N3b	2.133(7)	Ni2-N5	2.077(7)
Ni1-N4	2.051(7)	Ni2-N6c	2.097(7)
Ni1-N10	2.112(6)	Ni2-N7	2.094(8)
Ni1-N13	2.133(7)	Ni2-N13	2.141(8)
Ni1-O1	2.067(8)	Ni2-O2	2.045(7)

Bond angles			
Ni1-N13-Ni2	114.3(3)	Ni1-N4-N3-Ni1b	15.2
Ni1-N10-Ni1b	108.0(4)	Ni1-N3b-N4b-Ni1b	15.2
Ni2-N7-Ni2b	109.5(6)	Ni2-N5-N6-Ni2b	13.3
Ni1-N4-N5-Ni2	1.0	Ni1-N6b-N5b-Ni1b	13.3

[a] Symmetry-operations: a: 0.25-*x*, *y*, 1.25-*z*; b: 0.25-*x*, 1.25-*y*, *z*; c: *x*, 1.25-*y*, 1.25-*z*.

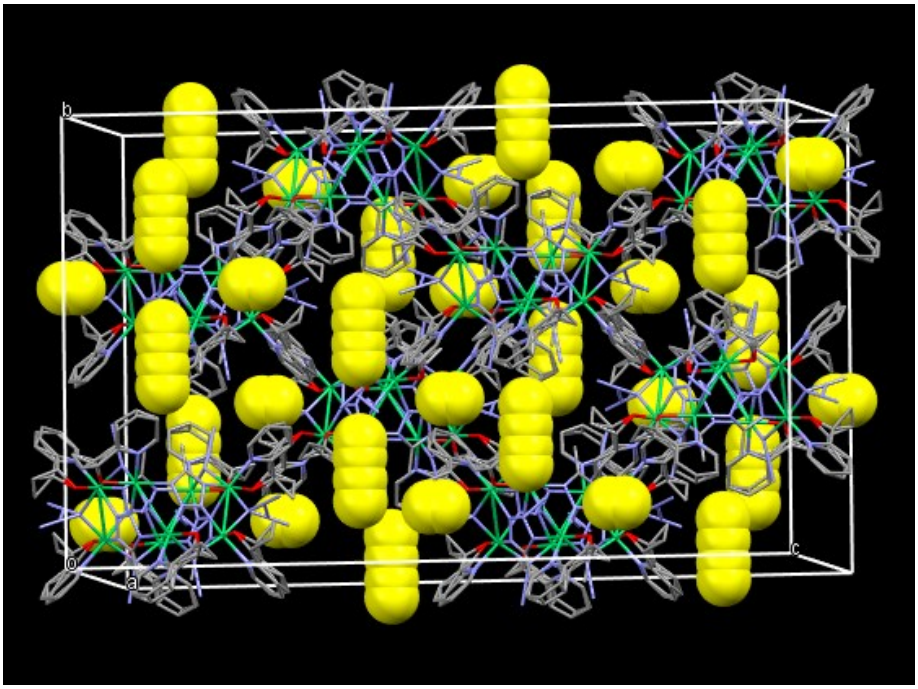

Fig. S1 Packing diagram of **1**·2.2H_2O. The lattice H_2O molecules are shown in yellow space-filling representation, emphasizing their tendency to occupy the voids between adjacent {Ni_8} clusters. Color scheme for the remaining atoms as in Fig. 1 of the main text.

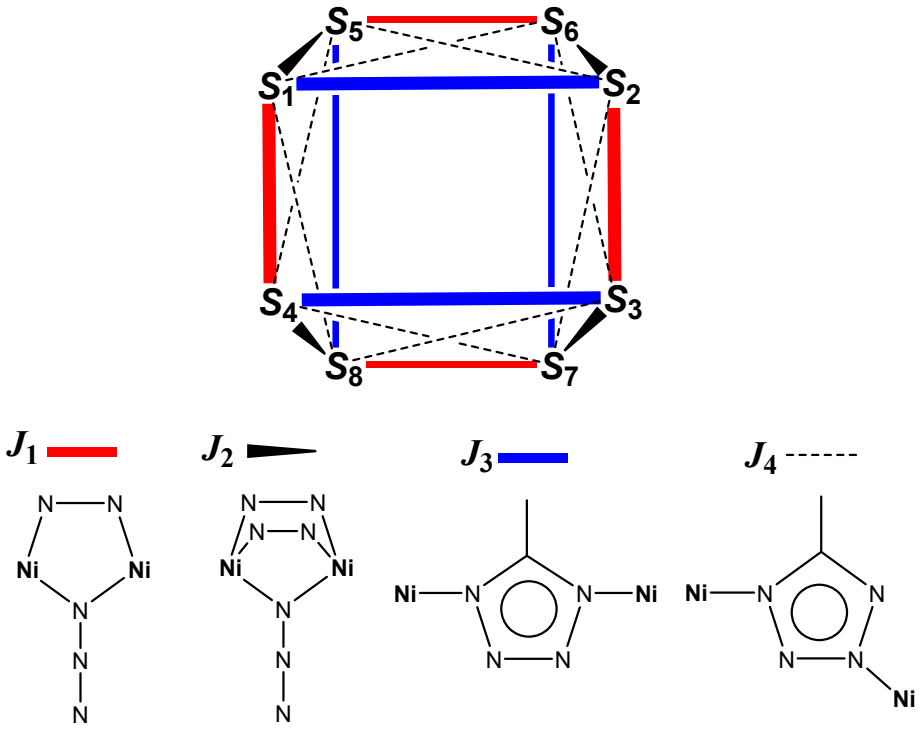

Fig. S2 Coupling scheme and the four superexchange pathways used to describe the magnetic exchange interactions in complex **1**.

Additional Magnetic Discussion. Based on the employed spin Hamiltonian (see eqn (1) in the main text), we performed several fits in order to check the influence of each coupling constant in the fitting procedure, neglecting selectively one of the interactions at a time. Despite the obtained good results for the susceptibility data, these alternative fits gave unreliable values of poor magneto-chemical sense for the J coupling constants, such as a larger ferromagnetic interaction for J_2 (compared to J_1) or different signs for J_1 and J_2, to name a few. The only case in which the negligence of a J-coupling constant gave good susceptibility and magnetization fits, as well as reasonable magneto-chemical results for the remaining parameters, is that of J_2 (see Table S3, red colored raw).

Table S3. J values (cm^{-1}) and R quality factor for the attempted additional fits, neglecting selectively one of the coupling constants at a time.

Excluded J constant	J_1	J_2	J_3	J_4	g	$R(\chi_M T)$	$R(M)$
J_1	**0.0**	+7.8	-1.6	-1.0	2.21	$4.2 \cdot 10^{-5}$	$4.8 \cdot 10^{-2}$
J_2	+11.5	**0.0**	-1.7	-1.3	2.18	$3.2 \cdot 10^{-5}$	$1.4 \cdot 10^{-3}$
J_3	-2.8	+7.7	**0.0**	-0.3	2.20	$3.0 \cdot 10^{-5}$	$5.4 \cdot 10^{-2}$
J_4	+0.9	+7.9	-3.8	**0.0**	2.20	$1.8 \cdot 10^{-5}$	$4.8 \cdot 10^{-2}$

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