SUPPORTING INFORMATION

Ferromagnetic Interactions in an Unusual 2D Coordination Polymer Including Di-2-pyridylketone, (1,1)-Azide, and Rare (1,1,3,3)-Azide Bridging Ligands

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S1. Experimental: Synthesis, Elemental Analysis, Experimental Procedures.

Synthesis and Analysis of **1.** The synthesis of **1** was carried out in a diffusive cell with three compartments. The wing compartments contained (right) an aqueous solution of $Cu(NO_3)_2.3H_2O$ (0.5 mmol) and (left) a methanolic solution of dpk (0.5 mmol) and NaN_3 (0.5 mmol), while the central one contained a mixture of methanol and water (1:1). After several days, prismatic, green, X-ray quality single crystals (43% yield) were obtained in both the central and right compartments. Anal. Calced for $C_{12}H_{11}N_{11}O_2Cu_2$: Cu, 27,13; C, 30.77; H, 2.37; N, 32.89. Found: Cu, 26,8; C, 30.5; H, 2.6; N, 33.0.

*Physical Measurements***.** Microanalyses were performed with a LECO CHNS-932 analyzer. Analytical measurements were carried out in an ARL 3410 + ICP with a Minitorch equipment. IR spectroscopy was performed on a Nicolet 520 FTIR spectrophotometer in the 400-4000 cm^{-1} region. Magnetic susceptibility measurements of powdered samples were carried out in the temperature range 4.2-300 K, at a value of the magnetic field of 0.1 T, using a Quantum Design MPM5-7 SQUID magnetometer, equipped with a helium continuous-flow cryostat. The experimental susceptibilities were corrected for the diamagnetism of the constituent atoms (Pascal tables). Magnetization measurements were carried out at 5 K and 10 K at increasing values of the magnetic field up to 7 T.

S2. IR spectra for compound 1 and dpk Ligand.

Table S1. Significant data of the IR spectrum of $[Cu_4(dpk.OCH_3)_2(N_3)_6]_n$ and of the organic di-2-piridilketone ligand.

	Di-2-piridilketone (dpk) (cm^{-1})	**$[Cu_4(dpk.OCH_3)_2(N_3)_6]_n$ (cm^{-1})**
Organic ligand		
υ(CO)	1680s	1603s
υ(C=C), υ(C=N)	1578s, 1565m	1580m
υ Pyridine ring	998m	980m
C-H out-of-plane bending	753s, 742s	780m, 765m
pyridyl ring in-plane vibration	662m	650m
Azide ligand		
$\upsilon_{as}(N_3)$		2090s, 2050s
$\upsilon_{s}(N_3)$		1340w,o
$\delta(N_3)$		647m

s= strong, m= medium, w= weak, o= overlap

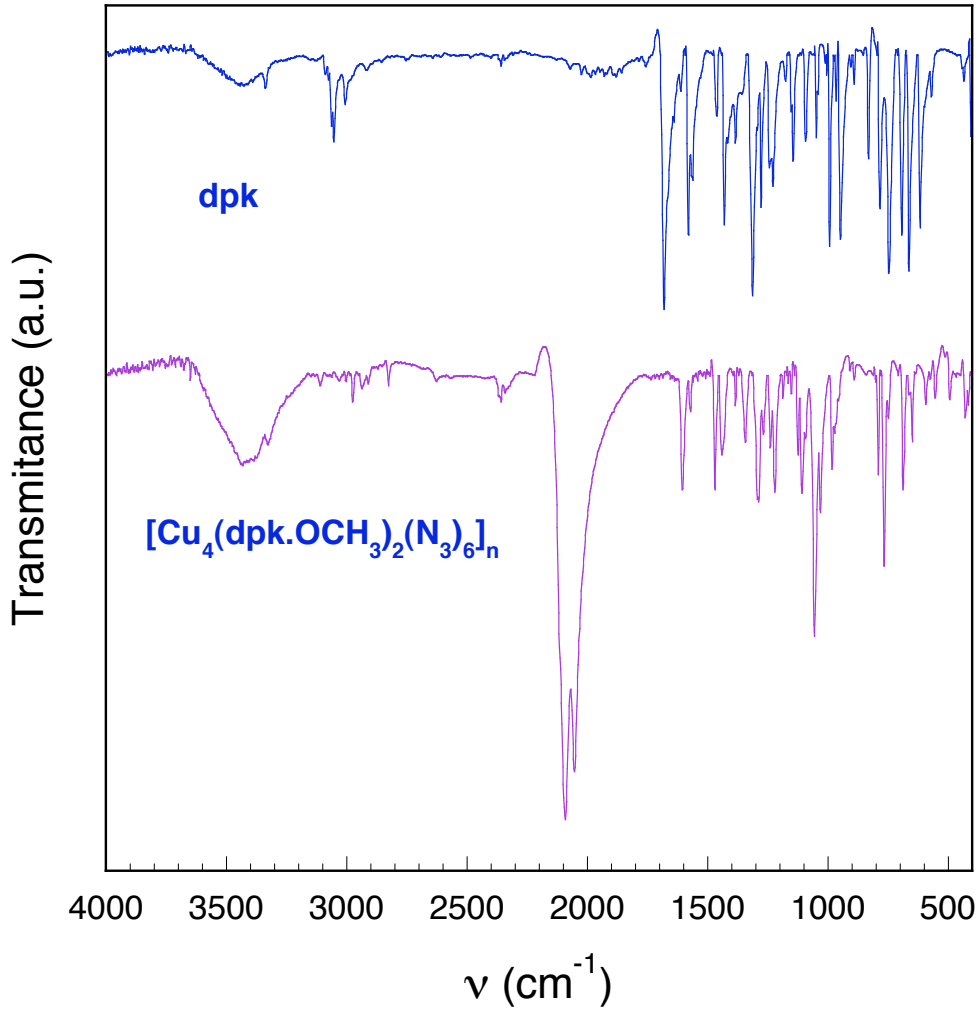

Figure S1. IR spectra of $[Cu_4(dpk.OCH_3)_2(N_3)_6]_n$ and of dpk ligand.

S3. Different structural views.

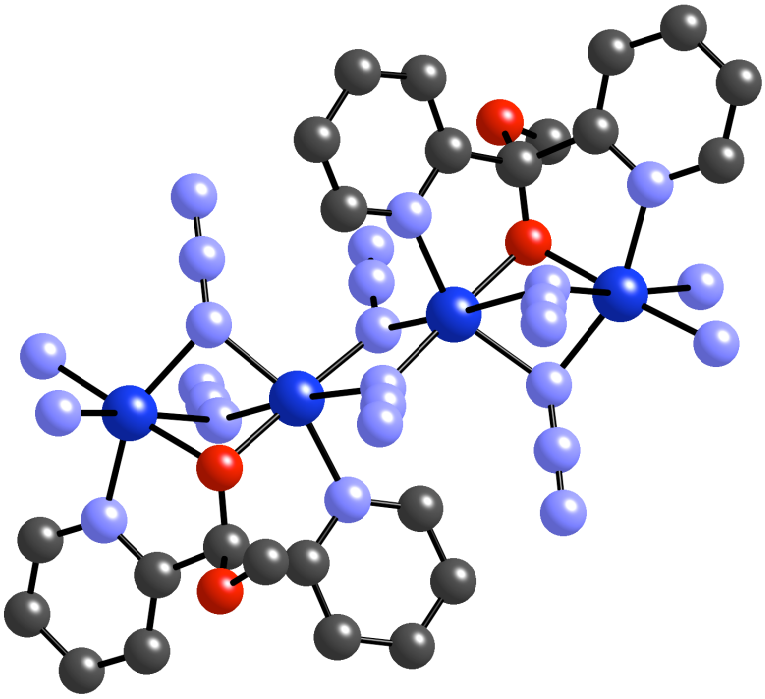

Figure S2. Global connection in each copper(II) ion in the tetramer.

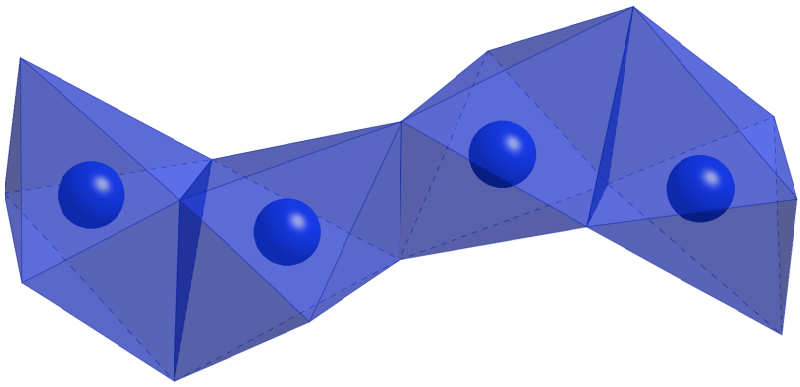

Figure S3. Distorted octahedral disposition in the tetramer.

S4. Different structural views.

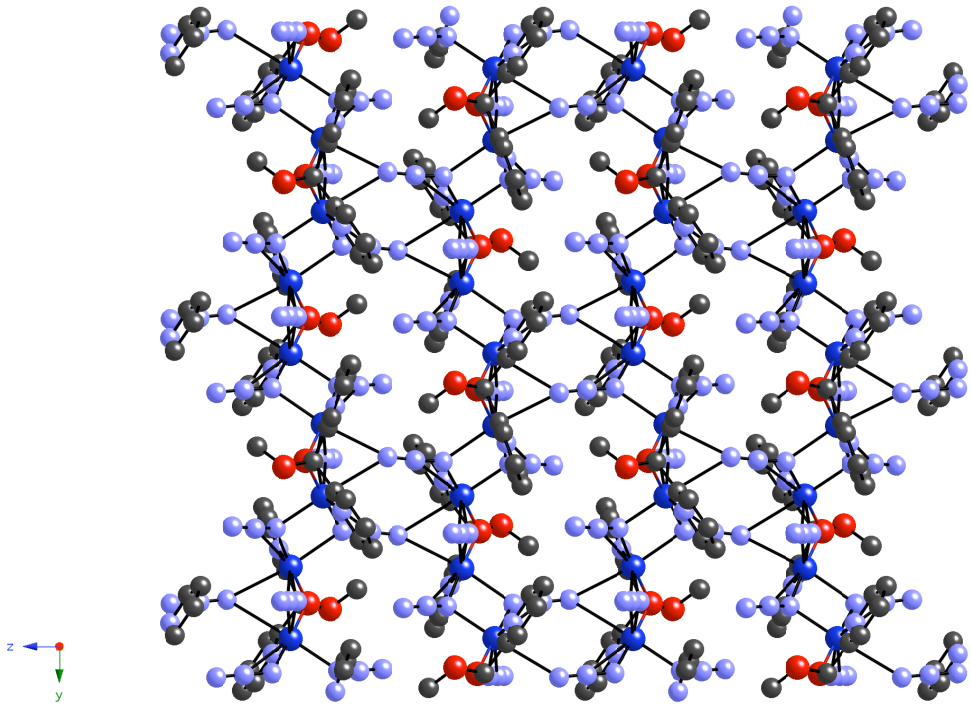

Figure S4. Global 2D structure in the (100) plane.

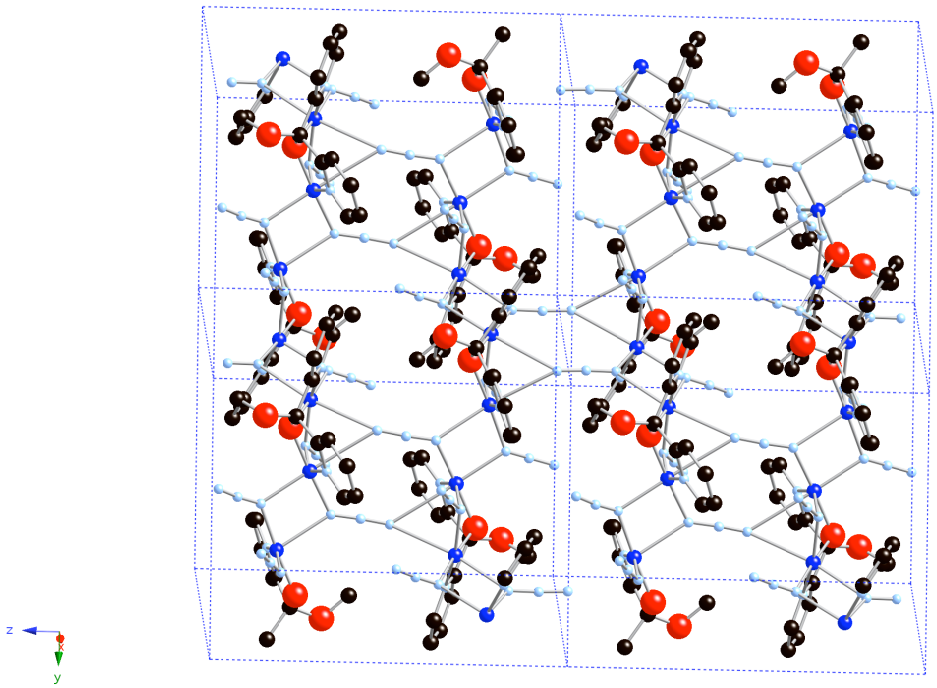

Figure S5. Disposition of 2D structure in the cell.

S5. Tentative fits to magnetic models.

- Exchange constant J for dimers with S=1/2[a]: solid magenta line in Figure S. Eq. 1:

$$\chi_m = \frac{Ng^2\beta^2}{3kT}\frac{1}{1+\frac{\exp(-2J/kT)}{3}} \qquad (1)$$

- Dimer + interdimeric exchange as an interdimer molecular field[b]: green discontinuous line. Eq. 2:

$$\chi = \frac{\chi_m}{(1-\frac{2k}{Ng^2\beta^2}zJ'\chi_m)} \qquad (2)$$

- Dimer + low-temperature antiferromagnetic exchange as an interdimer molecular field[c]: discontinuous red line

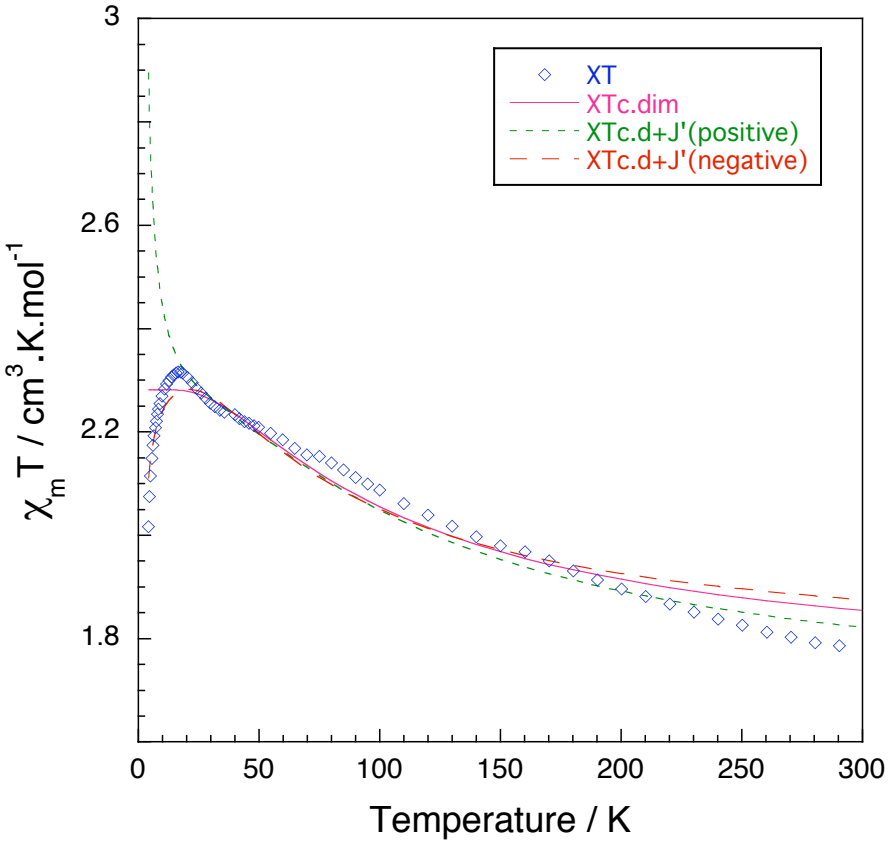

Figure S6. Tentative fits to indicate models (per 4 copper(II) ions).

*All expressions based upon the Hamiltonian: $H = -2J \sum S_1S_2$

[a] Bleaney, B.; Bowers, K. D. *Proc. R. Soc. London Ser. A*, **1952**, *214*, 451.
[b] Shen, Z.; Zuo, J.-L.; Yu, Z.; Zhang, Y.; Bai, J.-F.; Che, C.-M.; Fun, H.-K.; Vittal, J. J.; You, X.-Z. *J. Chem. Soc. Dalton Trans.* **1999**, 3393-3398.
[c] Shen, Z.; Zuo, J.-L.; Gao, S.; Song, Y.; Che, C.-M.; Fun, H.-K.; You, X.-Z. *Angew. Chem., Int. Ed.* **2000**, *39*, 3633-3635.