Electronic Supplementary Material (ESI) for Chemical Communications

Touching the upper limit for ferromagnetic interactions in hetero-bridged dinuclear [Cu^{II}_2] complexes using a novel N_5-dinucleating ligand bearing an endogenous monoatomic amido(R-NH^-)-bridging group.

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A) Experimental

General: Unless stated otherwise, reactions were conducted in oven-dried glassware upon aerobic conditions, and the reagents were purchased at the highest commercial quality being used without previous purification.

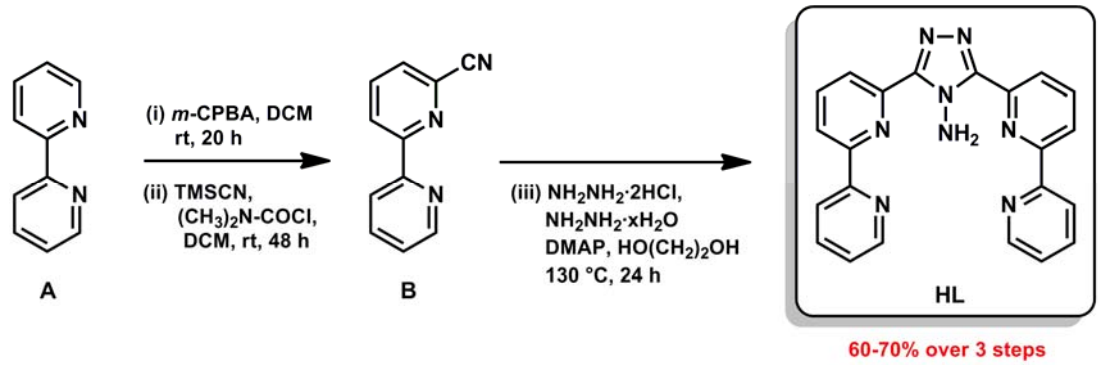

Figure S1. Schematised synthesis of the ligand (HL).

The two-step conversion of 2,2´-bispyridine (**A**) into the nitrile derivative (**B**) and the subsequent condensation leading to the corresponding 4-amine-1,2,4-triazole (**HL**), were carried out according to procedures previously described in the literature.[1,2]

[HL] IR (KBr) υ_{max} (cm^{-1}), 3386 , 3312 (s) and 3234 (**NH, s**), 3091, 3058, 3016 and 2929 (w, C-H_{arom}), 2883, 1581 and 1564 (s, **NH**), 1464, 1421, 1375, 1325, 1265, 1147, 1097, 1067, 1045, 1022, 993; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38 (2H, dd, ^3J = 4.8 Hz, ^4J = 0.9 Hz, 2x C-5´(***H***)), 7.87 (2H, td, ^3J = 7.8 Hz, ^3J = 7.7 Hz, ^4J = 1.7 Hz , 2x C-4´(***H***)), 8.03 (2H, t, ^3J = 7.9 Hz, 2x C-4(***H***)), 8.29 (2H, d, ^3J= 7.9 Hz, 2x C-5(***H***)), 8.41-8.49 (4H, m, 2x C-3(***H***) and 2x C-3´(***H***)), 8.53 (2H, s, -N***H₂***), 8.73-8.76 (2H, m, C-6(***H***)); **^{13}C NMR** (63 MHz, $CDCl_3$) δ 121.1 (**C**H), 122.1 (**C**H), 123.3 (**C**H), 124.3 (**C**H), 137.2 (**C**H), 138.6 (**C**H), 147.4 (**C**), 148.1 (**C**),

[1] T. Norrby, A. Börje, L. Zhang, B. Åkermark, *Acta Chemica Scandinavica*, 1998, **52**, 77.
[2] F. Bentiss, M. Lagrenée, M. Traisnel, B. Mernari, H. Elattari, *J. Heterocyclic. Chem.,* 1999, **36**,149.

149.8 (**C**H) 155.4 (**C**), 155.5 (**C**); Anal. Calcd (Found) for $C_{22}H_{16}N_8$ (**HL**): C, 67.34 (67.01); H, 4.11 (3.93); N, 28.55 (29.06).

Synthesis of the complexes 1–3:

$[Cu_2(\mu\text{-}L)(\mu\text{-}OH)(\mu\text{-}NO_3)(NO_3)]\cdot 5H_2O$ 1 To a stirred acetonitrile solution (30 mL) of 4-amine-1,2,4-triazole (**HL**) (79 mg, 0.2 mmol) and copper nitrate (97 mg, 0.4 mmol) was added distilled water (*ca.* 10 mL) until complete dissolution of the observed slurry. The resulting mixture was stirred upon gentle heating at 60-70 °C for 30 min and the subsequent greenish-blue solution was allowed to cool down, filtered off and allowed to stand undisturbed at room temperature for a week to furnish green crystals of **1** suitable for X-ray diffraction analysis which were collected by filtration and air-dried. **IR** (KBr) υ_{max} (cm^{-1}), 3431, 3216, 3067, 1595, 1563, 1519, 1479, 1433, 1400, 1387, 1339, 1254, 1169;

$[Cu_2(\mu\text{-}L)(\mu\text{-}N_3)(CH_3CN)(\mu\text{-}CF_3SO_3)(CF_3SO_3)]$ 2 .To a stirred acetonitrile solution (30 mL) of 4-amine-1,2,4-triazole (**HL**) (79 mg, 0.2 mmol) and copper triflate (145 mg, 0.4 mmol) was added distilled water (*ca.* 5 mL). The resulting mixture was stirred for 10 min at 60-70 °C and then NaN_3 (26 mg, 0.4 mmol) was added and the mixture was stirred for a further period of 20 min. Then the resulting dark navy-blue solution was allowed to cool down, filtered off and allowed to stand undisturbed at –5 °C for three weeks before obtaining dark navy-blue crystals of **2** suitable for X-ray diffraction analysis which were collected by filtration and air-dried. **IR** (KBr) υ_{max} (cm^{-1}), 3447, 3221, 3080, 2068, 1599, 1568, 1519, 1481, 1437, 1288, 1235, 1153, 1097, 1025;

$[Cu_2(\mu\text{-}L)(SCN)_3(H_2O)]\cdot H_2O$ 3 To a stirred acetonitrile solution (20 mL) of 4-amine-1,2,4-triazole (**HL**) (79 mg, 0.2 mmol) and copper triflate (145 mg, 0.4 mmol) was added distilled water (*ca.* 20 mL). The resulting mixture was stirred for 10 min at 60-70 °C and then KSCN (39 mg, 0.4 mmol) was added and the mixture was stirred for a further period of 20 min. Then the resulting dark green solution was allowed to cool down, filtered off and allowed to stand undisturbed at room temperature for three weeks to furnish dark green crystals of **3** suitable for X-ray diffraction analysis which were collected by filtration and air-dried. **IR** (KBr) υ_{max} (cm^{-1}), 3395, 2074, 2009, 1637, 1474, 1384, 1333, 1255, 1158;

B) Physical measurements

Elemental analyses were performed using a VarioEl III elemental analyzer. Magnetisation and variable temperature (2–300 K) magnetic susceptibility measurements on polycrystalline

samples were carried out with a Quantum Design SQUID MPMS XL-5 device operating at different magnetic fields. The experimental susceptibilities were corrected for the diamagnetism of the constituent atoms by using Pascal's tables.

C) X-ray data collection and structure refinement

Crystallographic data were collected at 123 K for **1**–**3** with a Nonius-Kappa CCD area-detector diffractometer using graphite monochromatised Mo-Kα radiation (λ = 0.71073 Å). The data were collected by ϕ and ω rotation scans and processed with the DENZO-SMN *v*0.93.0 software package.[3] Empirical absorption corrections were performed with SADABS program.[4] The structures were solved by direct methods using the SHELXS-97 or SIR-97 program[5] and full-matrix, least-squares refinements on F^2 were performed using the SHELXL-97 program[6] with the WinGX graphical user interface.[7] Thermal ellipsoid plots were obtained by using the DIAMOND program.[8] The partial packing diagrams were drawn with the MERCURY program.[9] All non hydrogen atoms for complexes **1–3** were refined anisotropically. The NH, OH and H_2O hydrogen atoms of **1–3** were located from the difference Fourier map and were refined isotropically while other hydrogen atoms were constrained to ride on their parent atoms. The crystal data for **1–3** along with other experimental details are summarised in the following table (Table S1).

[3] Z. Otwinowski and W. Minor, *Meth. Enzymol.,* 1997, **276**, 307-326.
[4] G. M. Sheldrick. SADABS, v.2.03, Bruker Area Detector Absorption and other Corrections.
[5] G. M. Sheldrick, SHELXS-97 and SHELXL-97: A Program for Crystal Structure Refinement, University of Göttingen, Germany, 1997; A. Altomare, M. Cascarano, C. Giacovazzo, A. Guagliardi, M. C. Burla, G. Pilodori, M. Camalli, *J. Appl. Crystallogr.* 1994, **27**, 435
[6] G. M. Sheldrick, *Acta Crystallogr. A,* 2008, **64**, 112-122.
[7] L. J. Farrugia, *J Appl Crystallogr,* 1999, **32**, 837.
[8] Diamond - Crystal and Molecular Structure Visualization v3.1f. Crystal Impact, K. Brandenburg & H. Putz GbR, Bonn, Germany, 2008.
[9] C. F. Macrae, P. R. Edgington, P. McCabe, E. Pidcock, G. P. Shields, R. Taylor, M. Towler and J. van de Streek, *J. Appl. Crystallogr.,* 2006, **39**, 453-457.

Table S1. Summary of crystallographic data for structures **1–3**

Complex	**1**	**2**	**3**
Chemical formula	$C_{22}H_{26}Cu_2N_{10}O_{12}$	$C_{26}H_{18}Cu_2F_6N_{12}O_6S_2$	$C_{25}H_{19}Cu_2N_{11}O_2S_3$
Formula Mass	749.61	899.72	728.77
Crystal system	Triclinic	Monoclinic	Triclinic
a/Å	7.2424(2)	15.2701(7)	8.1051(2)
b/Å	12.4631(4)	12.6225(7)	11.3327(2)
c/Å	15.7040(4)	18.4419(8)	15.9497(3)
α/°	82.150(2)	90	72.0390(10)
β/°	85.467(2)	114.855(3)	87.5780(10)
γ/°	78.319(2)	90	83.1160(10)
Unit cell volume/Å^3	1373.19(7)	3225.4(3)	1383.56(5)
Temperature/K	123 (2)	173(2)	123(2)
Space group	*P-1*	*P21/c*	*P-1*
Formula units per unit cell (*Z*)	2	4	2
Radiation type	MoKα	MoKα	MoKα
Absorption coefficient, μ/mm^{-1}	1.633	1.547	1.812
No. of reflections measured	17808	14588	16608
No. of independent reflections	5055	6252	5378
R_{int}	0.0476	0.0671	0.0338
Final R_1 values ($I > 2\sigma(I)$)[a]	0.0378	0.0605	0.0338
Final $wR(F^2)$ values ($I > 2\sigma(I)$)[b]	0.0772	0.1228	0.0742
Final R_1 values (all data)	0.0514	0.0967	0.0437
Final $wR(F^2)$ values (all data)	0.0823	0.1390	0.0784
Goodness of fit on F^2	1.052	1.027	1.032

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$.
[b] $wR_2 = \{\sum[w(F^2_o - F^2_c)^2]/\sum[w(F^2_o)^2]\}^{1/2}$ and $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP)]$, where $P = (2F^2_c + F^2_o)/3$.

D) Computational details

All theoretical calculations were carried out at the DFT level of theory using the hybrid B3LYP exchange-correlation functional,[10] as implemented in the Gaussian 03 program.[11] A quadratic

[10] A. D. Becke, *Phys. Rev. A: Gen. Phys.,* 1988, **38**, 3098-3100; C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B: Condens. Matter,* 1988, **37**, 785-789; A. D. Becke, *J. Chem. Phys.,* 1993, **98**, 5648-5652.
[11] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, Jr Montgomery J. A., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople. *Gaussian 03, Revision C.02*; Gaussian, Inc.: Wallingford CT, 2004.

convergence method was employed in the SCF process.[12] The triple–ζ quality basis set proposed by Ahlrichs and co-workers has been used for all atoms.[13] Calculations were performed on the complexes built from the experimental geometries. The electronic configurations used as starting points were created using the Jaguar 7.6 software.[14] The approach used to determine the exchange coupling constants for polynuclear complexes has been described in detail elsewhere.[15]

[12] G. B. Bacskay, *Chem. Phys.,* 1981, **61**, 385-404.
[13] A. Schäfer, C. Huber and R. Ahlrichs, *J. Chem. Phys.,* 1994, **100**, 5829-5835.
[14] *Jaguar 7.6*; Schrödinger, Inc.: Portland OR, 2009.
[15] E. Ruiz, J. Cano, S. Alvarez and P. Alemany, *J. Comput. Chem.,* 1999, **20**, 1391-1400; E. Ruiz, S. Alvarez, A. Rodriguez-Fortea, P. Alemany, Y. Pouillon and C. Massobrio, *Magn. : Mol. Mater. II,* 2001, , 227-279; E. Ruiz, A. Rodriguez-Fortea, J. Cano, S. Alvarez and P. Alemany, *J. Comput. Chem.,* 2003, **24**, 982-989; E. Ruiz, S. Alvarez, J. Cano and V. Polo, *J. Chem. Phys.,* 2005, **123**, 164110/1-164110/7.