THE UNIVERSITY of EDINBURGH

Edinburgh Research Explorer

Touching the upper limit for ferromagnetic interactions in hetero-bridged dinuclear [Cu-2(II)] complexes using a novel N-5-dinucleating ligand bearing an endogenous monoatomic amido(R-NH-)-bridging group

OPEN ACCESS

Download date: 05. Apr. 2019

Touching the upper limit for ferromagnetic interactions in hetero-bridged dinuclear [Cu_2^{II}] complexes using a novel N_5-dinucleating ligand bearing an endogenous monoatomic amido(R–NH⁻)-bridging group**

Enrique Colacio,[1,]* Jesús E. Perea-Buceta,[1] Antonio J. Mota,[1,]* Euan K. Brechin,[2]
Alessandro Prescimone,[2] Mikko Hänninen,[3] Petri Seppälä[3] and Reijo Sillanpää[3]

[1]Departamento de Química Inorgánica, Facultad de Ciencias, Universidad de Granada, Avda de Fuentenueva s/n, 18002-Granada, Spain.

[2]EaStCHEM, School of Chemistry, Joseph Black Building, University of Edinburgh, West Mains Road, Edinburgh, EH9 3JJ, UK.

[3]Department of Chemistry, University of Jyväskylä, P.O. Box 35, Jyv, Finland.

[*]Corresponding author; e-mail: ecolacio@ugr.es; fax: +34 958 248526 ; tel: +34 958 243236

Abstract

The novel N_5-dinucleating ligand 4-amino-3,5-bis(bipyridine-2-yl)-1,2,4-triazol   allows the preparation for the first time and in mild conditions of single and mixed amido(R-NH$^-$)-bridged copper(II) complexes, the latter exhibiting very strong ferromagnetic coupling.

Introduction

Polynuclear metal complexes bearing either amido (R,R'-N- or R-NH-)1-16 or hydrazido (R,R'-N-N2- or R, R'-N-NH-)17-18 monoatomic bridging ligands are rather rare species, most of them organometallic in nature, that have been prepared under drastic anaerobic reaction conditions. Amongst amido-bridged polynuclear complexes containing paramagnetic metal ions1-13 those that were magneto-structurally studied 5-8, 11-13 invariably showed antiferromagnetic interactions between metal ions. In view of this, more examples of this kind of polynuclear complex are needed in order to perform detailed theoretical and experimental studies on the ability of the amido-bridging ligands to mediate magnetic exchange interactions. We have synthesized a new symmetric N5-dinucleating ligand, namely 4-amino-3,5-bis(bipyridine-2-yl)-1,2,4-triazol (hereafter HL, Figure 1) specifically designed to prepare amido-bridged dinuclear complexes in mild aerobic reaction conditions.
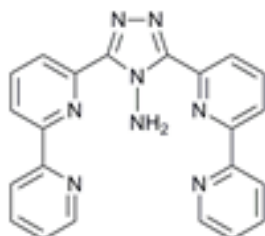
Figure 1. The dinucleating ligand HL

The ligand is rather rigid and imposes some geometric restrictions to the metal ions in the dinucleating cavity. Thus, the coordination of two metal ions to the nitrogen atoms of the bipyridine moieties should induce the deprotonation of the amino group, allowing it to act as a bridge between the metal ions and generating single amido-bridged dinuclear species with higher thermodynamic stability. In these species, the metal ions should simultaneously or subsequently saturate their remaining in-plane ligand positions with the donor atom(s) of a size-matching bridging ligand and the axial positions with donor atoms belonging to either bridging or ancillary ligands, ultimately leading

to heterobridged dinuclear metal complexes. These types of complexes, particularly those containing copper(II) ions, have received much attention for their interesting and diverse magnetic properties, which are in general due to the cooperation effect of the different bridging ligands (namely orbital complementarity and countercomplementarity).[19] Orbital countercomplementarity, together with magnetic orbital orthogonality, spin-polarization, double-exchange and crossed-interactions are the most important mechanisms for producing ferromagnetic interactions between metal ions.[20] It should be noted that although a huge number of polynuclear paramagnetic complexes exhibiting magnetic exchange interactions between metal centres have been reported so far, in only a few are the interactions ferromagnetic in nature. The achievement of ferromagnetic coupling between metal ions in polynuclear metal complexes is an interesting challenge for synthetic chemists not only because of its relative scarcity but also because it leads to high spin ground states, one of the most important requirements, together with the existence of a large negative axial anisotropy, for a cluster metal complex to exhibit single molecule magnet (SMM) behaviour.[21] Moreover, chains of ferromagnetically coupled axial anisotropic spins may behave as single-chain magnets (SCM).[22] These two kinds of systems, SMMs and SCMs are of current interest in chemistry and material science due to their potential applications in data storage and quantum computing. In view of the above considerations, we decided to explore the ability of the HL ligand to form single amido-bridged as well as in plane μ-amido/μ-X heterobridged dinuclear copper(II) complexes (X = OH, N_3^-) in mild conditions. In addition, the magnetic properties of these compounds were experimentally and theoretically studied to determine the magnitude and nature of the magnetic coupling mediated by the amido group.

Thus, the reaction of the of HL with $Cu(NO_3)_2 \cdot 3H_2O$ in a acetonitrile/water mixture and using a HL/Cu = 1:2 molar ratio led to the complex $[Cu_2(\mu\text{-L})(\mu\text{-OH})(\mu\text{-NO}_3)(NO_3)] \cdot 5H_2O$ 1. The same reaction but using $Cu(CF_3SO_3)_2$ and either NaN_3 or water crystallization molecules connected by an intricate network of hydrogen bonds involving the oxygen atoms of the coordinated nitrates, the N14 and N15 nitrogen atoms of the triazole moiety and the hydroxo bridging ligand, with donor-aceptor distances in the 2.786-3.020 Å range. Copper(II) ions present different coordination spheres, [4 + 2] for Cu1 and [4 + 1] for Cu2. Four short in-plane bonds of about 2.0 Å are formed in both cases by three N atoms (two from a bispyridine moiety and one from the deprotonated 4-amino bridging group) and the O atom belonging to the hydroxo-bridging group. The remaining axial and apical positions on the copper(II) ions are occupied by oxygen atoms belonging to the *syn-syn* bidentate and monodentate coordinated nitrate anions at longer distances ranging from 2.328 Å to 2.521Å (see Figure 2). The Cu⋯Cu distance is rather short, 2.8244(4) Å, and the Cu1-N18-Cu2 and Cu1-O1-Cu2 angles in the Cu(ON)Cu bridging fragment are 92.07(9) and 92.4(1)°, respectively. The hinge angle (γ) of the bridging fragment (measured as the dihedral angle between the Cu1-N-Cu2 and Cu1-O1-Cu2), is about 35.0°. As expected, the triazole plane is not coplanar with the bipyridine planes but forming a

dihedral angle (φ) of 24.17º. The structure of **2** (Figure 2) is rather similar to that of **1**, and it consists of neutral $[Cu_2(\mu\text{-}L)(\mu\text{-}N_3)(CH_3CN)(\mu\text{-}CF_3SO_3)(CF_3SO_3)]$ molecules with in-plane amido and end-on azido bridging groups, whereas two triflate anions (bidentate and monocoordinated) and one acetonitrile molecules are now occupying the axial, leading [4 + 2] coordination spheres. The Cu···Cu distance is somewhat larger than in **1** (2.952 Å) and, consequently, the Cu1-N18-Cu2 the Cu1-N2-Cu2 angles increase to 98.7(2)° and 93.3(2)°, respectively, whereas the γ and φ angles decrease to 12.97° and 14.15º, respectively. Complex **3** is made of a single amido-bridged $[Cu_2(\mu\text{-}L)(SCN)_3(H_2O)]\cdot H_2O$ dinuclear molecules and one water crystallization molecule. Within the dinuclear unit, three N-thiocyanate ligands and a water molecule occupy the apical positions on the dissimilar [4 + 1] copper(II) coordination spheres. The basal planes for Cu1 and Cu2 ar formed by three nitrogen atoms from the ligand and one nitrogen atoms from the SCN^- group with Cu-N distances of about 2.A, whereas the apical positions are filled by a water molecule in Cu1 and a SCN^- group KSCN in a HL/Cu/X = 1:2:2 molar ratio, led to complexes $[Cu_2(\mu\text{-}L)(\mu\text{-}N_3)(CH_3CN)(\mu\text{-}CF_3SO_3)(CF_3SO_3)]$ **2** and $[Cu_2(\mu\text{-}L)(SCN)_3(H_2O)]\cdot H_2O$ **3**, respectively (see Supporting Information).
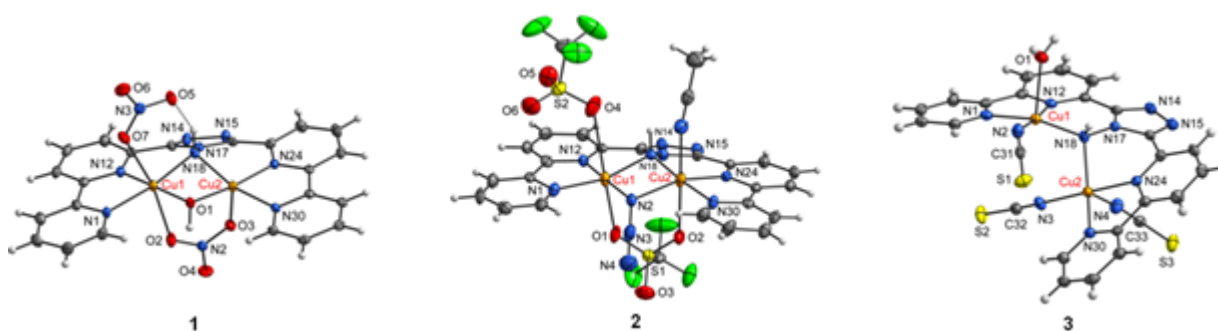
Figure 2. Perspective views of the structures of compounds **1**, **2** and **3**. Ellipsoids are drawn at the 50% probability

Complex **1** (see Figure 2) is made from neutral dinuclear heterobridged $[Cu_2(\mu\text{-}L)(\mu\text{-}OH)(\mu\text{-}NO_3)(NO_3)]$ units and five in Cu2, at longer distances. In the crystal, dinuclear molecules are held together in pairs by a couple of complementary and centrosymmetrically related N14…O1 hydrogen bonds. The existence of only one bridging ligand in the structure gives rise to an increase of Cu···Cu distance (3.376 Å) and the Cu1-N18-Cu2 angle (115.23(11)°). To avoid the steric hindrance promoted by the SCN- anions coordinated in basal positions, the copper(II) coordination planes are turned to each other by 58.80 º.

The temperature dependences of $\chi_M T$ for complexes **1**–**3** (χ_M is the molar magnetic susceptibility per Cu_2 unit) in an applied magnetic field of 1 T are displayed in Figure 3. The $\chi_M T$ products at room

temperature for heterobridged complexes **1** and **2** are 1.028 and 0.99 cm^{3}Kmol^{-1}, respectively, which are somewhat above the expected values for two magnetically isolated doublets. These values continuously increase on cooling to reach a maximum value at 45 K of *ca* 1. 146 and 1.371 cm^{3}Kmol^{-1} for **1** and **2**, respectively, and further decrease at lower temperatures to a value of *ca.* 0.9 cm^{3}Kmol^{-1}. The shape of this curve is typical of a relatively strong ferromagnetic interaction, the decrease of $\chi_M T$ at low temperature being ascribed to intermolecular interactions and/or zero-field splitting effects (ZFS). The magnetic data were analyzed using a Bleaney-Bowers equation with the inclusion of the ZFS (D) and a parameter (zJ') to account intermolecular interactions through the molecular-field approximation. Best-fit parameters were: J = 185(4) cm^{-1}, g = 2.149(1), D = 0 cm^{-1} and zJ' = -0.37(1) cm^{-1} for **1** and J = 212(8) cm^{-1}, g = 2.141(1), D = 0.8(1) cm^{-1} and zJ' = -0.26(2) cm^{-1} for **2**. For 3, the $\chi_M T$ product steadily decreases when the temperature is lowered to reach a plateau at *ca.* 25 K with a value close to zero. This behaviour is due to a medium to strong antiferromagnetic interaction between the copper(II) ion through the amido bridging group. The best fit to the Bleaney-Bowers equation led to following parameters: J = -92(1) cm^{-1} and g = 2.069 (1). Preliminary DFT theoretical calculations on the single-amido bridged model compound [Cu$_2$(μ-L')(NH$_3$)$_6$] (L' = 4-amino-triazol) predict ferromagnetic interactions for Cu-N-Cu bridging angle (θ) values within the 90º-114º range. The *J* value decreases with the θ angle reaching an antiferromagnetic regime for $\theta \geq 114$º. In **3**, the Cu-N-Cu angle is larger than 114º and, therefore, an antiferromagnetic interaction is expected, which match well with the experimental results for this compound. In compounds **1** and **2** with θ angles much lower that 114º, the amido-bridge is expected to mediate ferromagnetic interactions. The Cu-X-Cu bridging angles for hydroxo and azido bridged in **1** and **2** of 92.07° and 93.3°, respectively, also promote ferromagnetic coupling.[22] Therefore, both bridging ligands (amido and X) transmit ferromagnetic interactions between the copper(II) ions. As far as we know, this is the first time that this fact is observed in heterobridged copper(II) complexes. Only a few examples of ferromagnetically coupled heterobridged dinuclear copper(II) have been reported so far, and in all of them the ferromagnetic interactions are caused by orbital countercomplementarity (the two bridges counterbalance their effects) either between two bridges with AF contributions or with F/AF contributions.[19, 23] In view of this, the fact that compounds **1** and **2** exhibit the largest ferromagnetic interactions ever observed for heterobridged dinuclear copper(II) complexes (and comparable to the larger found for homodinuclear (II) complexes,[24] see table 1) is not unexpected.
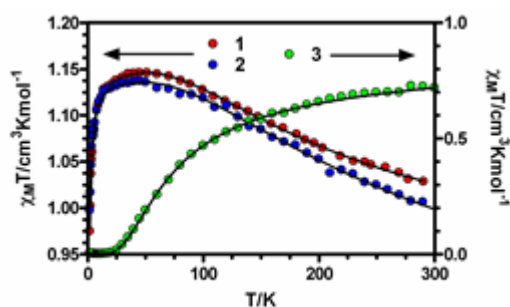
← *Figure 3.* Temperature dependences of $\chi_M T$ for **1** and **2** (left axis) and **3** (right axis). Solid lines correspond to the best fits.

DFT calculations performed on the crystal structures of complexes **1**–**3** agree quite well with the experimental results, supporting the high F coupling observed for complexes **1** and **2** and the AF interaction mediated by the amido bridging group in compound **3** (see table 1). DFT calculations also show that the third bridge connecting axial positions on the copper(II) ions in **1** and **2** (nitrate and triflate) do not have any significant influence on the J value, as expected for long Cu-O_{axial} bond lengths and negligible spin density of the unpaired electron on the axial positions.

Compound	Experimental	Theoretical
1	+185	+190.3
2	+210	+195.8
3	−91.85	−17.7
$[Cu_2(\mu-1,1-N_3)_2(4\text{-Etpy})_4(\mu\text{-}NO_3)_2]$ [a]	+230.1(1)	+138.9
$[Cu_2(\mu-1,1-N_3)_2(3\text{-ampy})_4(\mu\text{-}NO_3)_2]$ [a]	+223.2(2)	+195.3

[a] The highest ferromagnetic values reported so far for Cu2 complexes.[24] 4-Etpy = 4-ethylpyridine. 3-ampy = 3-aminopyridine

Table 1. Compared experimental and theoretical J values (in cm^{-1}).

In summary, a novel N_5-dinucleating ligand has been specifically designed to prepare amido-bridged metal complexes. We have succeeded in obtaining for the first time and in mild conditions, single and mixed amido-bridged dinuclear copper(II) complexes. The mixed-bridged complexes, in which both bridges connecting equatorial or basal positions on the copper(II) atoms (amido and either hydroxo or azido) mediate F interactions, exhibit the largest ferromagnetic couplings ever observed for this kind of compounds. Deeper theoretical and experimental studies on single and mixed-bridged complexes with this ligand and different metal ions are in progress.

References

[1] W. H. Monillas, G. P. A. Yap, K. H. Theopold, *J. Chem. Crystallogr*, 2009, **39**, 535.

[2] A. A. Danopoulos, G. Wilkinson, T. K. N.Sweet, M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, 1996, 271.

[3] C. Weymann, A. A. Danopoulos, G. Wilkinson, *Polyhedron*, 1996, **15**, 3605.

[4] C. S. Alvarez, A. Bashall, A. D. Bond, D. Cave, E. A. Harron, R. A. Layfield, M. E. G. Mosquera, M. McPartlin, J. M. Rawson, P. T. Wood, D. S. Wright, *Dalton Trans.*, 2003, 3002 and references.

[5] A. Malassa, C. Agthe, H. Görls, M. Podewitz, L. Yu, C. Herrmann, M. Reiher, M. Westerhausen, *Eur. J. Inorg.Chem.*, 2010, 1777.

[6] C. R. Hamilton, R. A. Baglia, A. D. Gordon, and M.l J. Zdilla, *J. Am. Chem. Soc.* 2011, **133**, 4208.

[7] Y. Takemura, T. Nakajima, T.Tanase, M. Usuki, H. Takenaka,

[8] E. Goto and M. Mikuriyab, *Chem. Commun.* 2009, 1664.

[9] X. Xiaofeng, J. Guili S. Hongjian, L. Xiaoyan, *Z. Anorg. Allg. Chem.* 2011, **637**, 430.

[10] R. A. D. Soriaga, S. Javed, D. M. Hoffman *J. Clust. Sci.* 2010, **21**, 567.

[11] J. A. Hatnean, R. Raturi, J. Lefebvre, D. B. Leznoff, G. Lawes, S. A. Johnson, *J. Am. Chem. Soc.* 2006, **128**, 14992.

[12] C. Ni, G. J. Long, F. Grandjean, P. P. Power, *Inorg. Chem.* 2009, **48**, 11594.

[13] M..-L. Tong, C.-G. Hong, L.-L. Zheng, M.-X. Peng, A. Gaita-Ariño, J. M. C. Juan, *Eur. J. Inorg.Chem.*, 2010, 1777.

[14] S. Kannan, A.J. James, P.R. Sharp Polyhedron 2000, **19**, 155.

[15] R. Dorta, A. Togni, *Helv. Chim. Acta*, 2000, **83**, 119.

[16] A. L. Keen, M. Doster, H. Han and S. A. Johnson, , Chem. Commun. 2006, 1221.

[17] C. Redshaw, S. Jana, C. Shang, M. R. J. Elsegood, X. Luc and

[18] Z. X. Guo, Chem. Commum. 2010, 46, 9055

[19] J. A. Cabeza, I. del Rıo, J. M. Fernández-Colinas, E. Pérez-Carreñoo, D. Vázquez-García, *Organometallics* 2010, **29**, 4818.

[20] a) V. McKee, M. Zvagulis, J. V. Dagdigian, M. G. Patch, C. A. Reed, *J. Am. Chem. Soc.*, 1984, **106**, 4765. b) L.-L.Wang, Y.-M. Sun, Z.-N. Qi, C.-B. Liu, *J. Chem. Phys. A*. 2008, **112**, 8418 and references.

[21] a) O. Khan, *Molecular Magnetism*, VCH, Weinheim, Germany, 1993. b) E. Pardo, R. Carrasco, R. Ruiz-García, M. Julve, F. Lloret, M.C. Muñoz, Y. Journaux, E. Ruiz and J. Cano, *J. Am. Chem. Soc.*, 2008, **130**, 576.

[22] G. Aromí, E. K. Brechin,. *Struct. Bonding* (Berlin) 2006, **122**, 1.

[23] H. Miyasaka,, M. Julve, M. Yamashita, R. Cléerac, *Inorg. Chem.* 2009**, 48**, 3420

[24] E. Ruiz, S. Alvarez, A. Rodríguez-Fortea, P. Alemany, Y. Pouillon, C. Massobrio, *in Magnetism: Molecules to Materials II*; Ed. J. S. Miller and M. Drillon; WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim, 2001; Chapter 7, page 277.

[25] R. Costa, I. P.R. Moreira, S. Youngme,, K. Siriwong, N. Wannarit, Francesc Illas, Inorg. Chem. 2010, **49**, 285.

[26] A. Escuer, M. A. S. Goher, F. A. Mautner, R. Vicente, *Inorg. Chem.*, 2000, **39**, 2107.