Substituted *m*-phenylene bridges as strong ferromagnetic couplers for Cu^{II}–*bridge*–Cu^{II} magnetic interactions: new perspectives†

Alok Ranjan Paital,[b] Tamoghna Mitra,[b] Debashis Ray,*[b] Wing Tak Wong,[c] Jordi Ribas-Ariño,[d] Juan J. Novoa,[d] Joan Ribas[a] and Guillem Aromí*[a]

Received (in Cambridge, UK) 19th July 2005, Accepted 31st August 2005
First published as an Advance Article on the web 13th September 2005
DOI: 10.1039/b510074g

Based on a combined theoretical–experimental study, we propose that substituted *m*-phenylene ligands (*m*-N-Φ-N) can act as tuneable strong ferromagnetic couplers connecting Cu^{II} ions; a new complex presenting that bridge with *J* close to +15 cm^{-1} has been suggested and synthesized.

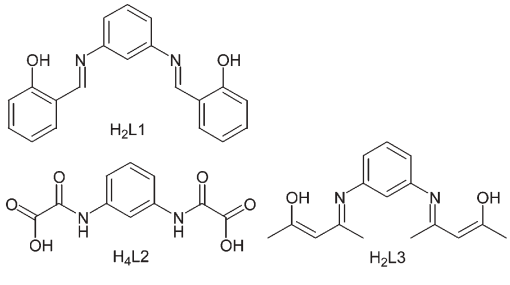
In molecular magnetism the deliberate inclusion of ferromagnetism is a synthetic challenge.[1] This has been attempted by exploiting magnetic-exchange through orthogonal (accidental or not) magnetic orbitals or through the so called spin polarization mechanism,[1–3] among other modes. However, the true challenge is not only to force the existence of ferromagnetic coupling, but also being able to increase its strength. This can be done by identifying bridging ligands known to act as ferromagnetic couplers and establishing the properties that lead to an enhancement of the interaction, eventually synthesizing the improved systems.

Here we focus our attention on the capability of diamagnetic substituted *m*-phenylene (*m*-N-Φ-N) ligands to act as ferrocouplers between Cu^{II} ions. Contradictory magnetic data exist in the literature for ligands of this type, their behaviour being reported as an antiferro- or ferromagnetic coupler. We have analyzed experimentally and theoretically the capacity of such a moiety to mediate magnetic interactions and have found it to be an efficient ferromagnetic coupler in most cases. We predicted and then synthesized a new system exhibiting efficient ferromagnetic exchange, measured to be of +15 cm^{-1}. Furthermore, following a comprehensive theoretical study, we predict that *J* values of up to +325 cm^{-1} could be obtained when the appropriate *m*-N-Φ-N ligand is used. Such exchange would be greater than any ferromagnetic coupling reported to date between ions, including those linked by monoatomic bridges such as with end-on N_3^-, halides or OR^- bridging ligands ($J \cong +90$ cm^{-1} for an N_3^- bridge).[4]

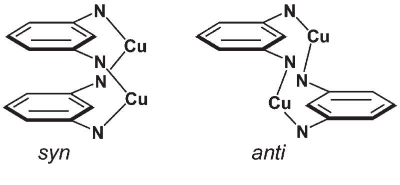
As early as 1978, Hendrickson and coworkers reported a singular binuclear distorted Cu^{II} complex, $[Cu_2(L1)_2]$ (**1**, H_2L1 in Scheme 1) with a geometry between square planar, SP and tetrahedral, T_d, for which weak antiferromagnetic coupling was claimed ($J = -1.0$ cm^{-1} in the $H = -JS_1S_2$ convention).[5] Against such a finding, the synthesis and magnetic properties of a structurally analogous binuclear Cu^{II} complex, $Na_4[Cu_2(L2)_2]$ (**2**, H_4L2 in Scheme 1) have been recently reported.[6] Interestingly, the copper centers within **2** show efficient ferromagnetic coupling ($J = +16.8$ cm^{-1}, in the same convention for the spin-Hamiltonian as for **1**). Such a difference in magnetic behaviour is intriguing, as in both cases the bridging ligand is a substituted *m*-phenylene. The ferromagnetic coupling in **2** occurs, according to the authors, *via* a spin-polarization phenomenon, mediated through the bridging π-system. Inspection of these two similar, but magnetically disparate, complexes allows one to appreciate two major structural differences between them: (i) the *m*-phenylene rings in **1** are parallel to each other but mutually shifted, precluding any π–π interaction (*anti* in Scheme 2), whereas these rings are stacked in **2** (*syn* in Scheme 2); (ii) the Cu^{II} ions have a geometry half way between SP and T_d in **1** but SP in **2**.

If the spin-polarization was the main mechanism creating the ferromagnetism, it seems clear that the relative positions of the two *m*-phenylene bridges (stacked *vs.* shifted) would not be important. Thus, the question arises as to whether the disparity in magnetic behaviour is due to the difference in coordination geometry of Cu^{II} or whether other factors are important.

DFT calculations were used in order to obtain insights into this problem. For complex **2**, such studies had already been



Scheme 1



Scheme 2

---

[a] *Departament de Química Inorgànica, Universitat de Barcelona, Diagonal, 647 08028-Barcelona, Spain. E-mail: guillem.aromi@qi.ub.es; Fax: +34 93 490 7725; Tel: +34 93 402 1271*
[b] *Department of Chemistry, Indian Institute of Technology, Kharagpur 721 302, India. E-mail: dray@chem.iitkgp.ernet.in; Fax: 91-3222-82252; Tel: 03222-283324*
[c] *Department of Chemistry, University of Hong Kong, Pokfulam Road, Pokfulam, Hong Kong SAR, P. R. China. E-mail: wtwong@hkucc.hku.hk; Fax: 852-2547-2933; Tel: 852-2859-7914*
[d] *Departament de Química Física and CERQT, Universitat de Barcelona, Diagonal, 647 08028-Barcelona, Spain*
† Electronic supplementary information (ESI) available: Figs. S1–S4. See http://dx.doi.org/10.1039/b510074g

Table 1 Models used to calculate the influence of the ligand on *J via* the *m*-phenylene bridge

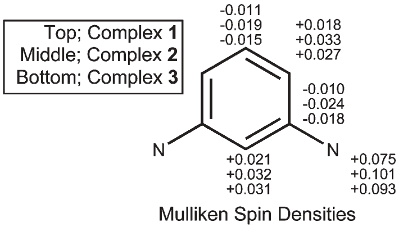
Model	Geometry	Ligand	J/cm^{-1}	$\Sigma|\rho_i|$
A	Complex **1**	H_2L1	+1.7	0.239
B	Complex **1**	H_2L3	+7.5	0.287
C[a]	Complex **1**	$R_1 = R_2 = R_3 = H$	+4.4	0.283
D[a]	Complex **1**	$R_1 = F, R_2 = R_3 = H$	+12.3	0.283
E[b]	optimized	Scheme 5 a	+39.1	0.471
F[b]	optimized	Scheme 5 b	+325.2	1.111
G	Complex **3**	H_2L3	+14.5	0.322

[a] Positions 1, 2 and 3 are those indicated on Scheme 4. [b] In these models the geometry of the complexes was first optimized.

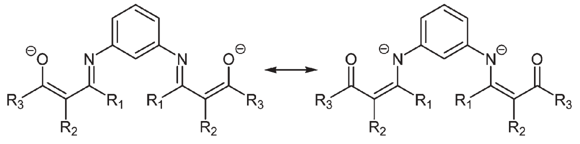
performed,[6] and the results were in very good agreement with the experimental magnetic data. We carried out DFT calculations on complex **1**[7] using the B3LYP functional[8] and an Ahlrich's pVDZ basis set.[9] The broken-symmetry procedure was used to evaluate the singlet state energy. The *J* value as obtained from [E(Tr) − E(BSS)] (Tr, triplet; BSS, broken symmetry singlet)[10] was small but ferromagnetic ($J_{calc.} = +1.7$ cm^{-1}, see Table 1, **A**). The small discrepancy with the experimental value previously reported could be because the model used for fitting the experimental data of **1** did not include possible intermolecular interactions.[11] Inspection of the Mulliken population analysis (Scheme 3) reveals that spin densities on the central linker are lower in **1** compared to **2**. This fact suggests a connection between the spin population on the atoms of the bridge and the intensity of ferromagnetic coupling, which can be influenced by changing the ligand structure.

We performed further DFT calculations to explore how the magnetic coupling is affected by the electronic structure of the ligand. These calculations were done on a series of model complexes obtained by preserving the *m*-N-Φ-N part of the ligand as in **1**, while changing the lateral groups. The aim was to increase the charge on the N-donor atom, by favoring the resonance form that does this (right form in Scheme 4).

The systems explored and the results obtained are given in Table 1 (see also Fig. S1†). For the most part, substituents that favour charge localization on the N-atom lead to a larger *J* (as high as +325 cm^{-1}). A good correlation is found between *J* and the sum of absolute values of the atomic spin population on the atoms of the *m*-N-Φ-N moiety ($\Sigma|\rho_i|$) (Table 1; Fig. S2†). A higher transfer of spin density is associated with a better interaction between the HOMO orbitals of the bridging ligand and the SOMO orbitals of the copper(II) ions.



Scheme 3



Scheme 4

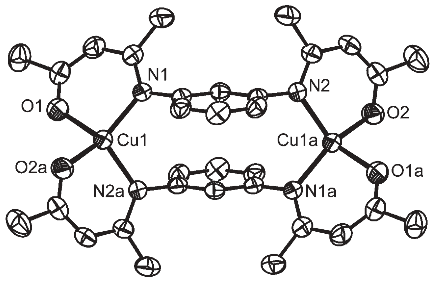


Fig. 1 ORTEP (50%) of $[Cu_2(L3)_2]$ (**3**). H-atoms are not shown. Only non C-atoms are labeled. Cu–O: 1.912(3) and 1.907(3) Å; Cu–N: 1.958(3) and 1.962(3) Å; N–Cu–N: 105.6(1)°; O–Cu–O: 88.3(1)°; O–Cu–N: 94.1(1) to 145.2(1)°. Atoms labelled 'a' have been generated with [−x,−y,−z].

Experimental support for the validity of this theoretical prediction was obtained from the synthesis of a new dinuclear copper(II) complex using the ligand H_2L3 (Scheme 1) already known in the literature.[12] A $[Cu^{II}_2]$ complex of this ligand was predicted in the above calculation to have enhanced ferromagnetism ($J = +7.5$ cm^{-1}, model **B** in Table 1). The reaction of H_2L3 with $[Cu_2(O_2CMe)_4{\cdot}2H_2O]$ in 1 : 1 molar ratio in methanol affords the compound $[Cu_2(L3)_2]$ (**3**)‡ as purple crystals.§ Ligand $L3^{2-}$ bridges and chelates two Cu^{II} ions to form a centrosymmetric complex (Fig. 1) where the N_2O_2 environment around each Cu^{II} center is half way between SP and T_d. The intramolecular Cu···Cu distance in **3** is 7.266 Å, whereas the shortest intermolecular vector joining two metals is 6.98 Å. The *m*-phenylene rings of the ligands are parallel to each other but mutually shifted, as in the case of complex **1**.

The $\chi_M T$ *vs.* T plot of **3** (Fig. 2, χ_M is the molar paramagnetic susceptibility) at room temperature is 0.87 cm^3 mol^{-1} K, close to the value of two non-interacting Cu^{II} ions. Upon cooling, $\chi_M T$ increases to reach 1.01 cm^3 mol^{-1} K near 10 K and then decreases down to 0.77 cm^3 mol^{-1} K at 2 K. This shows that the Cu^{II} ions within **3** are coupled ferromagnetically, as theoretically expected. The decrease of $\chi_M T$ upon cooling below 10 K is due to either intermolecular interactions and/or zero-field splitting (ZFS). These low-temperature effects were not observed in previously reported

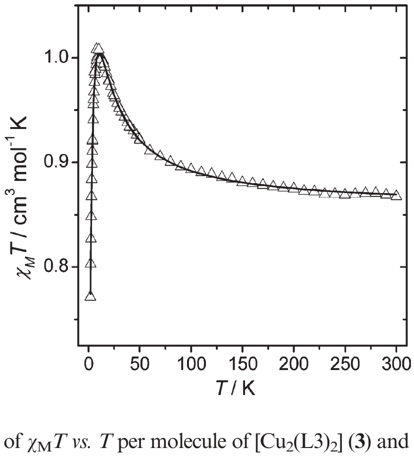


Fig. 2 Plot of $\chi_M T$ *vs.* T per molecule of $[Cu_2(L3)_2]$ (**3**) and fit (solid line, see text).

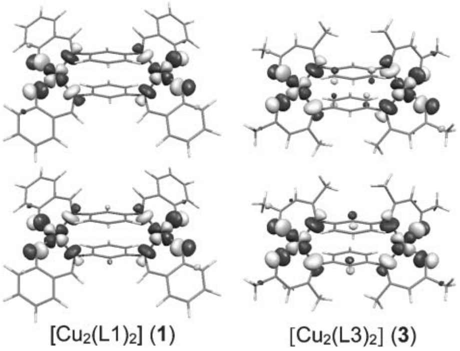
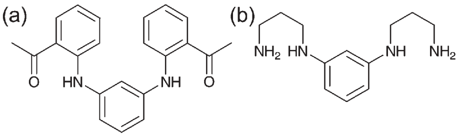

[Cu$_2$(L1)$_2$] (**1**) [Cu$_2$(L3)$_2$] (**3**)

Fig. 3 Representation of the two SOMOs for [Cu$_2$(L1)$_2$] (**1**) and [Cu$_2$(L3)$_2$] (**3**), from DFT calculations.

ferromagnetic complex **2**.[6] The magnetization data for **3**, at 2 K (Fig. S3†) are not matched by the Brillouin function for an $S = 1$ state with $g = 2.13$. The best simulation of the EPR spectrum of **3** gives negligible ZFS parameters (Fig. S4†). Thus, the pronounced decrease of $\chi_M T$ at low temperature must be due to intermolecular interactions. The presence of Na$^+$ ions in complex **2** separating the molecules might explain the differences between **2** and **3** in low temperature behaviour. The fit of the susceptibility data of **3** to the Bleaney–Bowers equation (for the Hamiltonian $H = -JS_1S_2$) gives $J = +14.56$ cm^{-1}, J' (intermolecular) $= -0.98$ cm^{-1} and $g = 2.13$ (in agreement with the EPR value). This coupling, exceptionally strong for two Cu$^{\text{II}}$ ions separated by 7.266 Å, is very similar to that reported for complex **2**,[6] where J is +16.8 cm^{-1} and the Cu···Cu distance is 6.8 Å. Also, it shows that the predicted trend for this ligand was correct. The fact that the experimental value is even higher than the predicted one indicates that the mere structural parameters might also have an influence on the calculated J. Indeed, a new DFT calculation now using the geometry as obtained crystallographically for **3** yielded $J = +14.5$ cm^{-1} (model **G** in Table 1), in perfect agreement with the value found experimentally. The Mulliken population analysis for **3** resulting from these new calculations (Scheme 3) shows again an increased presence of spin density on the linker with respect to complex **1**. In Fig. 3 are represented the two single occupied molecular orbitals (SOMOs) calculated for **1** and **3**, showing the difference in contribution of the aromatic bridge to the coupling.

From the above experimental and theoretical results it is concluded clearly that the electronic properties of the ligand have an important influence on the strength of the coupling, a fact that is manifested in the increased spin density on the atoms of the central link.

This study shows that a properly designed ligand system can provide access to enhanced ferromagnetism. Calculations using a model with a hypothetical ligand designed to greatly favour concentration of charge on the atoms taking part in the bridge, (*m*-phenylene-bis(1,3-diaminopropane), Scheme 5(b), Fig. S1†) predict J values as high as +325 cm^{-1}. In this case, there are not energetically attainable resonance forms allowing delocalization of the negative charge (generated upon deprotonation) to the outer parts of the ligand. Such strong ferromagnetic coupling between two copper(II) ions has never been observed experimentally up to now.



Scheme 5

In conclusion, DFT studies show that the *m*-N-Φ-N bridge in Cu$^{\text{II}}$–bridge–Cu$^{\text{II}}$ complexes is a (potentially) strong ferromagnetic coupler. An analysis of the spin density suggests that its efficiency is associated with the participation of the *m*-N-Φ-N part of the ligand of the molecular orbitals determining the spin distribution. This can be controlled experimentally by playing with the substituents attached to the backbone of the ligand using synthetic tools: the newly synthesized dinuclear copper(II) complex (**3**) proves the validity of this idea. Our theoretical predictions indicate that a good choice of the chelating moiety linked to the central benzene group would make it possible to reach J values of up to +325 cm^{-1}. A great challenge is thus now offered to experimental chemists.

Notes and references

‡ Elemental Anal. % Calcd (Found) for **3**: C, 57.56 (57.45); H, 5.43 (5.52); N, 8.39 (8.28).

§ Crystal data for **3**: $C_{32}H_{36}N_4O_4Cu_2$, M_w = 667.75, orthorhombic, *Pbca*, a = 8.969(2), b = 17.068(3), c = 19.951(4) Å, V = 3054.2(11) Å^3, Z = 4, D_c = 1.452 g cm^{-3}, μ = 1.435 mm^{-1}. R = 0.039, wR = 0.042. CCDC 265565. See http://dx.doi.org/10.1039/b510074g for crystallographic data in CIF or other electronic format.

1 O. Kahn, *Molecular Magnetism*, VCH, New York, 1993.
2 T. Ishida, S. Mitsubori, T. Nogami, N. Takeda, M. Ishikawa and H. Iwamura, *Inorg. Chem.*, 2001, **40**, 7059.
3 J. A. Crayston, J. N. Devine and J. C. Walton, *Tetrahedron*, 2000, **56**, 7829.
4 S. S. Tandon, L. K. Thompson, M. E. Manuel and J. N. Bridson, *Inorg. Chem.*, 1994, **33**, 5555.
5 E. F. Hasty, L. J. Wilson and D. N. Hendrickson, *Inorg. Chem.*, 1978, **17**, 1834.
6 I. Fernandez, R. Ruiz, J. Faus, M. Julve, F. Lloret, J. Cano, X. Ottenwaelder, Y. Journaux and M. C. Muñoz, *Angew. Chem., Int. Ed.*, 2001, **40**, 3039.
7 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., 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. 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. G. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople, *GAUSSIAN 03*, Gaussian, Inc., Wallingford, CT, 2004.
8 A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648.
9 A. Schafer, H. Horn and R. Ahlrichs, *J. Chem. Phys.*, 1992, **97**, 2571.
10 E. Ruiz, J. Cano, S. Alvarez and P. Alemany, *J. Comput. Chem.*, 1999, **20**, 1391.
11 D. Y. Jeter and W. E. Hatfield, *Inorg. Chim. Acta*, 1971, **6**, 440.
12 L. C. Nathan and C. A. Traina, *Polyhedron*, 2003, **22**, 3213.