

# Theoretical search for new ferromagnetically coupled transition metal complexes

Eliseo Ruiz,<sup>\*a</sup> Santiago Alvarez<sup>a</sup> and Pere Alemany<sup>b</sup>

<sup>a</sup> *Departament de Química Inorgànica, Universitat de Barcelona, Diagonal 647, 08028 Barcelona, Spain.*  
E-mail: eliseo@linus.ubi.es

<sup>b</sup> *Departament de Química Física, Universitat de Barcelona, Diagonal 647, 08028 Barcelona, Spain*

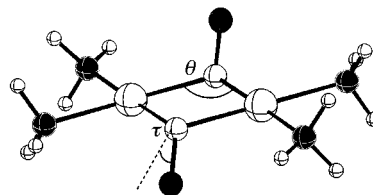
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Computational methods based on the density functional theory have been employed in the search for new ferromagnetic molecules and several compounds are predicted to exhibit stronger ferromagnetic coupling than the known hydroxo-bridged complexes, especially remarkable is the very strong coupling predicted for oxo-bridged Cu(II) or Ni(II) dimers.

One of the strategies applied to obtain new materials with interesting magnetic properties consists of increasing their structural dimensionality by combining binuclear building blocks to form chains, layers or tridimensional networks.<sup>1</sup> The choice of binuclear transition metal building blocks with different exchange coupling patterns opens up a number of possibilities in this area.<sup>2</sup> Hence, the magnetic behavior of a variety of such compounds has been explored during the last decades<sup>3</sup> with the aim of designing molecular magnets or molecule-based magnets. However, the large number of known antiferromagnetic complexes is in sharp contrast with the paucity of ferromagnetic systems. Up to now, the search for ferromagnetic coupling in binuclear transition metal complexes has been based on the synthesis of heteronuclear complexes with strictly orthogonal singly-occupied molecular orbitals (SOMOs) or of complexes with accidentally degenerate SOMOs. Theoretical studies are therefore of great help in establishing the factors that lead to such accidental degeneracy in a given compound.

In recent work<sup>4,5</sup> we have shown the ability of hybrid density functional-Hartree-Fock methods to provide good numerical estimates of the exchange coupling constant  $J$  (defined in the Heisenberg hamiltonian  $H = -JS_1S_2$ ) by using the B3LYP method<sup>6</sup> implemented in the GAUSSIAN package,<sup>7</sup> combined with a modified broken-symmetry approach.<sup>8</sup> The excellent results obtained so far prompted us to apply such methodology in search for new complexes with ferromagnetic behavior. A reasonable starting point for this search is to chemically modify Cu(II) systems already known to behave ferromagnetically, such as the hydroxo- or the end-on azido-bridged complexes. In particular, the hydrogen atom of the hydroxo bridging group offers a wider choice for chemical substitution. For hydroxo-bridged Cu(II) binuclear complexes, a classical correlation between the experimental exchange constant and the Cu–O–Cu bond angle  $\theta$  indicates that those complexes are antiferromagnetic for  $\theta > 98^\circ$ , but ferromagnetic for smaller angles.<sup>9</sup> In our previous work, we have shown that for these complexes the out-of-plane shift ( $\tau$ ) of the hydrogen atoms on the bridge also plays a crucial role in determining the magnetic behavior, since the ferromagnetic coupling increases with  $\tau$ .<sup>4,5</sup>

We started by analyzing the influence of the substituent at the oxygen atom on the value of  $J$ , using the model compounds  $[(\text{NH}_3)_2\text{Cu}(\mu\text{-OR})_2\text{Cu}(\text{NH}_3)_2]$  **1**, with the bond angles  $\theta$  and  $\tau$  fixed at  $101^\circ$  and  $0^\circ$ , respectively. From now on we will refer to this particular structure as geometry **A**. In spite of the antiferromagnetic character found for the hydroxo-bridged complexes with this structure, we compare the calculated value of  $J$  with that of the hydroxo derivative with the same geometry



as a criterion for selecting the best candidates. The calculated exchange constants for the different models with geometry **A**<sup>10</sup> are presented in Table 1, together with an indication of the pertinent structural data for the related compounds found in the Cambridge Structural Database (CSD).<sup>11</sup> From the calculated values of  $J$  some conclusions can be drawn: (1) all the alkoxy- and phenoxy-bridged complexes show stronger antiferromagnetic coupling than the hydroxo-bridged ones, in agreement with the experimental results. (2) For the methoxy-bridged compounds, substitution of the hydrogen atoms by alkyl groups weakens the antiferromagnetic coupling. (3) In general, the larger the electronegativity of the substituent, the stronger the antiferromagnetic coupling (*i.e.*, the values of  $-J$  appear in the order OF > OCR<sub>3</sub> > OH  $\approx$  OBR<sub>3</sub> > OSiR<sub>3</sub>  $\approx$  OGeR<sub>3</sub> > OAlR<sub>3</sub> > OLi), although there are a few exceptions to this rule. The effect of substituents at a distance of two bonds cannot be rationalized according to the same electronegativity criterion, as seen for the two R groups in OSiR<sub>3</sub> and OGeR<sub>3</sub>.

**Table 1** Calculated coupling constants ( $\text{cm}^{-1}$ ) for  $[(\text{NH}_3)_2\text{Cu}(\mu\text{-OR})_2\text{Cu}(\text{NH}_3)_2]^{n+}$  with structure **1** ( $n = 0$ , OR = O, OSO<sub>3</sub>, OBR<sub>3</sub> and OAlR<sub>3</sub>;  $n = 4$  for OR = OPy;  $n = 2$  for all other OR) in geometries **A** ( $\theta = 101^\circ$ ,  $\tau = 0^\circ$ ) and **B** ( $\theta = 96^\circ$ ,  $\tau = 50^\circ$ )

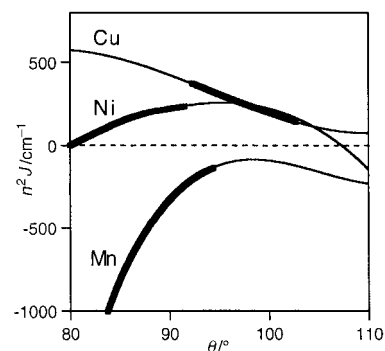
R	$J_{\text{calc}}$		$N^a$	$\theta/^\circ$	$\tau/^\circ$	$J_{\text{exp}}$
	<b>A</b>	<b>B</b>				
F	-1855	0				
Me	-778		14	98–104	2–48	
BH <sub>3</sub>	-687	+273	0			
Et	-669		31	96–105	2–44	-1064/-65
Bu <sup>t</sup>	-617		2	102–103	22–29	
Ph	-587		36	96–105	0–33	-852/-166
Py	-675		15	104–110	3–26	-855/-242
H	-493	-46	15	94–105	0–62	-509/+172
GeH <sub>3</sub>	-331	+5	0			
SiH <sub>3</sub>	-278	+19	0			
Ge(OH) <sub>3</sub>	-259	-36	0			
COMe	-230	-75	11	95–107	4–24	
NO <sub>2</sub>	-221	-58	1	106	13	
Si(OH) <sub>3</sub>	-202	-14	0			
Al(OH) <sub>3</sub>	-134	+137	0			
SO <sub>3</sub>	-108	+60	1	103	9	
SOMe	+8	-104	1	105	46	
Li	+100	+331	0			
—	+989	+782	0			

<sup>a</sup> The experimental structural data have been obtained with the help of the CSD.<sup>11</sup> The number ( $N$ ) indicates the structures with planar Cu<sub>2</sub>O<sub>2</sub> rings. An all electron double- $\zeta$  basis has been employed in the calculations.<sup>12</sup>

Since the angles  $\theta$  and  $\tau$  adopted in the model structure **A** are not expected to favor ferromagnetism, we selected the least antiferromagnetic or most ferromagnetic compounds for further exploration with a structure more likely to favor ferromagnetism. For them, a second set of calculations was performed with  $\theta$  and  $\tau$  fixed at 96 and 50°, respectively (geometry **B**), and the calculated coupling constants are also presented in Table 1. In practically all cases, the new geometry results in a decrease of the antiferromagnetic contribution, as expected for the smaller energy gap of the SOMOs obtained by reducing  $\theta$  while simultaneously increasing  $\tau$ .<sup>13</sup> The exceptions (O and OSOCH<sub>3</sub>) should be attributed to the fact that the energy ordering of the SOMOs is inverted in these compounds. As a consequence, the energy gap between these two orbitals increases with the Cu–O–Cu bond angle and a stronger antiferromagnetic contribution results.<sup>4</sup> From the calculated exchange constants, one can conclude that the sulfato and OX bridges with X = Li, BR<sub>3</sub>, AlR<sub>3</sub>, SiR<sub>3</sub> or GeR<sub>3</sub> could yield ferromagnetic complexes. Especially remarkable is the fact that the OBH<sub>3</sub>-bridged compound is made much more ferromagnetic upon changing its geometry from **A** to **B**. However, we could only detect one case of a related complex in the literature, having an OB(R)=O bridge and quite large Cu–O distances. In summary, our results indicate that copper(II) binuclear complexes bridged by oxygen bonded to an electropositive atom, such as an alkali, alkaline-earth, group 13 or group 15 element, are good candidates to present a strong ferromagnetic coupling. Notice that our prediction of ferromagnetic systems is based on a particular set of structural parameters ( $\theta = 96^\circ$  and  $\tau = 50^\circ$ ). Thus, we are investigating whether such structures are energetically feasible for the selected compounds by optimizing model structures of increasing complexity. Preliminary results show that the selected systems adopt structures close to that corresponding to geometry **B** and a strong ferromagnetic coupling should be expected.

A particularly surprising result is the exceptionally strong ferromagnetic coupling constants obtained for the oxo-bridged complex of copper (+989 and +782 cm<sup>-1</sup> for geometries **A** and **B**, respectively), as compared to the largest values reported in the literature for azido- and hydroxo-bridged complexes (+170 and +172 cm<sup>-1</sup>, respectively).<sup>14,15</sup> To obtain a more realistic model of an oxo-bridged complex, we have repeated the calculations adding an NH<sub>3</sub> ligand in the fifth coordination position of each copper atom, whereupon the calculated exchange constant for geometry **B** is reduced to +661 cm<sup>-1</sup>, exhibiting still a very strong ferromagnetic character, comparable to the calculated value (+685 cm<sup>-1</sup>) for the optimized structure of the penta-coordinate copper model. In agreement with the Hay–Thibeault–Hoffmann model,<sup>13</sup> all the oxo-bridged model calculations reveal a near-degeneracy of the two SOMOs. Unfortunately, no oxo-bridged Cu(II) complexes have been described in the literature to the best of our knowledge. An indication of the ability of the oxo bridge to induce ferromagnetic coupling is provided by the  $\mu$ -aqua- $\mu$ -oxo complex described by Chaudhuri *et al.*,<sup>16</sup> which is tautomeric to the corresponding bis( $\mu$ -hydroxo) complex. The latter presents a coupling constant of -90 cm<sup>-1</sup> whereas the former shows a ferromagnetic behavior with a singlet–triplet gap of +74 cm<sup>-1</sup>. Recently, Root *et al.* reported the structure of a trinuclear complex containing a Cu<sub>3</sub>O<sub>2</sub> core with two Cu(II) and one Cu(III) ion showing a singlet–triplet gap of +14 cm<sup>-1</sup>.<sup>17</sup>

Similar bis ( $\mu$ -oxo) complexes with transition metals other than copper have been described, mainly with manganese<sup>18,19</sup> and iron.<sup>20</sup> In sharp contrast to our theoretical prediction for copper, these complexes show antiferromagnetic coupling. To verify our predictions against the experimental data for Mn and Fe, we have studied the dependence of  $J$  on the angle  $\theta$  for the model complex [(NH<sub>3</sub>)<sub>4</sub>M( $\mu$ -O)<sub>2</sub>M(NH<sub>3</sub>)<sub>4</sub>], where M = Cu, Ni or Mn. The results, represented in Fig. 1, show a parabolic dependence of  $J$  on  $\theta$ , with the maximum value of  $J$  appearing at smaller angles in the order Mn > Ni > Cu, similar to that we previously found for the end-on azido-bridged complexes.<sup>21</sup>



**Fig. 1** Total exchange constants ( $n^2J$ , where  $n$  is the number of unpaired electrons per metal atom) for bis  $\mu$ -oxo complexes of Cu(II), Ni(II) and Mn(II) as a function of the bridging angle  $\theta$ . The outlined parts of the curves correspond to those geometries within 3 kcal mol<sup>-1</sup> of the calculated energy minima (1 cal = 4.184 J).

The main difference is that for the azido complexes ferromagnetic coupling is found for the three metals while the oxo-bridged Mn(II) complexes show antiferromagnetic behavior, consistent with the available experimental data for the d<sup>5</sup> Fe(III) oxo-bridged complex.<sup>20</sup> The values of the optimized  $\theta$  angles are also different for the two bridges with the same metal. Thus, for the end-on azido complexes the order Mn > Ni > Cu was found for such angle, whereas for the oxo-bridged complexes the largest value is that for Cu. As a conclusion, Ni(II) and Cu(II) complexes with an oxo bridge or with electropositive substituents at the bridging oxygen constitute interesting synthetic goals for new potentially ferromagnetic systems.

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