Inorg. Chem. **2003**, *42*, 4881–4884

Inorganic Chemistry
Article

Tailor-Made Strong Exchange Magnetic Coupling through Very Long Bridging Ligands: Theoretical Predictions

Eliseo Ruiz,* Antonio Rodríguez-Fortea, and Santiago Alvarez

Departament de Química Inorgànica and Centre Especial de Recerca en Química Teòrica,
Universitat de Barcelona, Diagonal 647, 08028 Barcelona, Spain

Received November 15, 2002

Computational methods based on density functional theory have been applied to a prospective study of dinuclear transition metal complexes that may show strong exchange coupling interactions through very long bridging ligands. The results indicate that M(III) complexes (being M= Cr, Mn or Fe) with dicyanamidobenzene-type ligands are specially promising for this purpose, since strong ferromagnetic or antiferromagnetic coupling is predicted between paramagnetic metal cations at distances as long as 25 Å. The existence of ferromagnetic or antiferromagnetic coupling in the complexes with the different isomers of dicyanamidobenzene can be rationalized in terms of molecular orbitals.

The synthesis of new polynuclear coordination compounds with interesting and new magnetic properties is one of the main goals in the field of molecular magnetism.[1] The magnetic behavior of a variety of dinuclear transition metal compounds has been explored to learn about the exchange interactions between two paramagnetic centers.[2] One of the strategies consists of searching for bridging ligands that would allow us to obtain a wide range of magnetic properties. However, the actual situation is far from ideal since the large number of known antiferromagnetic complexes is in sharp contrast with the paucity of ferromagnetic systems.[3] Usually, relatively small bridging ligands are employed in order to provide a short exchange pathway that favors a strong coupling. This fact introduces several limitations for the assembly of new complex systems; for instance, in the case of hybrid compounds obtained by host···guest inclusion, the short bridging ligands restrict the host lattices to those with rather small cavities.[4,5] The aim of this communication is to perform a theoretical search for new complexes with a very long exchange pathway, for which the exchange coupling could be tuned from ferromagnetic to antiferromagnetic by design.

During the last years, several authors have applied theoretical methods to study the exchange interactions in transition metal complexes.[6−11] In recent works,[12−16] we have shown the performance of the hybrid density functional B3LYP[17] method combined with the broken-symmetry approach to provide good numerical estimates of the exchange coupling constant J (introduced by the phenomenological Heisenberg Hamiltonian $H = -J{\cdot}S_1{\cdot}S_2$) by using the GAUSSIAN package[18] and an all electron basis set.[19,20] The use of the nonprojected energy of the broken symmetry solution as the energy of the low spin state within the DFT framework provides good results because it avoids the

---

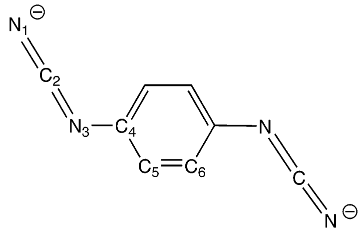
* To whom correspondence should be addressed. E-mail: eliseo.ruiz@qi.ub.es.

(1) Kahn, O. *Molecular Magnetism*; VCH Publishers: New York, 1993.
(2) *Magnetism: Molecules to Materials*; Miller, J. S., Drillon, M., Eds. Wiley-VCH: Weinheim, 2001.
(3) De Munno, G.; Julve, M.; Lloret, F.; Faus, J.; Verdaguer, M.; Caneschi, A. *Inorg. Chem.* **1995**, *34*, 157−165.
(4) Coronado, E.; Galán-Mascarós, J. R.; Gómez-García, C. J.; Martínez-Agudo, J. M. *Inorg. Chem.* **2001**, *40*, 113−120.
(5) Ballester, G.; Coronado, E.; Gimenez-Sáiz, C.; Romero, F. M. *Angew. Chem., Int. Ed.* **2001**, *40*, 792−795.
(6) Bencini, A.; Totti, F.; Daul, C. A.; Doclo, K.; Fantucci, P.; Barone, V. *Inorg. Chem.* **1997**, *36*, 5022−5030.
(7) Caballol, R.; Castell, O.; Illas, F.; Moreira, I. d. P. R.; Malrieu, J. P. *J. Phys. Chem. A* **1997**, *101*, 7860−7866.
(8) Nishino, M.; Yamanaka, S.; Yoshioka, Y.; Yamaguchi, K. *J. Phys. Chem. A* **1997**, *101*, 705−712.
(9) Noodleman, L.; Peng, C. Y.; Case, D. A.; Mouesca, J. M. *Coord. Chem. Rev.* **1995**, *144*, 199−244.
(10) Ruiz, E.; Alvarez, S.; Rodríguez-Fortea, A.; Alemany, P.; Pouillon, Y.; Massobrio, C. In *Magnetism: Molecules to Materials*; Miller, J. S., Drillon, M., Eds.; Wiley-VCH: Weinheim, 2001; Vol. 2, p 227−279 and references therein.
(11) Yamaguchi, K.; Tsunekawa, T.; Toyoda, Y.; Fueno, T. *Chem. Phys. Lett.* **1988**, *143*, 371−376.
(12) Ruiz, E.; Alemany, P.; Alvarez, S.; Cano, J. *J. Am. Chem. Soc.* **1997**, *119*, 1297−1303.
(13) Ruiz, E.; Alemany, P.; Alvarez, S.; Cano, J. *Inorg. Chem.* **1997**, *36*, 3683−3688.
(14) Ruiz, E.; Cano, J.; Alvarez, S.; Alemany, P. *J. Am. Chem. Soc.* **1998**, *120*, 11122−11129.
(15) Ruiz, E.; Cano, J.; Alvarez, S.; Alemany, P. *J. Comput. Chem.* **1999**, *20*, 1391−1400.
(16) Desplanches, C.; Ruiz, E.; Rodríguez-Fortea, A.; Alvarez, S. *J. Am. Chem. Soc.* **2002**, *124*, 5197−5205.
(17) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648−5652.

10.1021/ic026179r CCC: $25.00

cancellation of the nondynamic correlation effects as stated recently by Polo et al.[21,22] The details of the methodology employed are discussed with detail in a previous work.[15] The excellent results obtained so far prompted us to apply such methodology to predict the magnetic behavior of as yet unknown complexes.[23]

As a starting point we look for aromatic bridging ligands because of their ability to transmit electronic effects at long distance. An interesting candidate is 1,4-dicyanamidobenzene (1,4-dicyd) (**1**) that has been employed by Crutchley et al. in the synthesis of mixed valence ruthenium complexes.[24] Such compounds show a large comproportionation constant,[25] consistent with a class III mixed valence character according to the Robin-Day classification.[26] Furthermore, equivalent Ru(III) dinuclear complexes show diamagnetic behavior, indicative of a strong antiferromagnetic coupling.[27,28]



1

We have explored five transition metal ions, Ni(II), Fe(III), Mn(II), Mn(III), and Cr(III), with a pseudooctahedral coordination (**2**), in order to have unpaired electrons in the t_{2g} or in the e_g orbitals or in both. The *anti* conformation of the bridging ligand adopted by most of the ruthenium complexes (**1**) was used for the *para* dicyd ligand.[24] Since isomeric dinuclear complexes with bridges differing in the number of intervening bonds between the donor atoms may switch the exchange coupling from ferro- to antiferromagnetic, as demonstrated for bipyridine Mo compounds,[29] we have also performed calculations on the analogous systems with the *meta* dicyd ligand (**3**). For this ligand, there is no experimental structural information in transition metal complexes. We have performed calculations in order to compare the relative stability of *syn* and *anti* conformations of the free *meta* dicyd ligand, and we found the *syn* conformer to be 1.2 kcal/mol more stable than the *anti* one. This fact is not unexpected due to the steric hindrance of the *anti* conformer, and this difference of stability should be larger when the ligand is coordinated to a transition metal. The geometry optimizations performed for the transition metal complexes give unrealistic geometries, especially in the case of complexes with the 1,4-dicyd ligand where a linear structure for the NCNC atom sequence is found.

Recently, Tordini et al. studied the isomerization between the cyanamide and carbodiimide using DFT methods.[30] These authors explored the relative stability of the two isomers using several functionals, and in all cases, the stability of the carbodiimide form is overestimated. Consequently, in most cases, the carbodiimide form is calculated to be more stable than the cyanamide one, in contradiction with experiment. Although the use of hybrid functionals may give the right stability order, even the B3LYP functional with some basis sets gives the wrong order. The unrealistic linear structure that we found when optimizing the complex with the 1,4-dicyd ligand, using the B3LYP functional, corresponds to a sequence of the NCN atoms of the cyanamide type rather than the carbodiimide one found experimentally for the free ligand and for the ruthenium complex (see **1**). This fact can be attributed to the wrong estimation of the relative energy of this kind of systems by density functional theory with the functionals at hand. For that reason, we decided to adopt for our exploratory study the experimental structure of the 1,4-dicyd ligand in one of its ruthenium complexes,[31] while for the 1,3-dicyd ligand we have employed an equivalent structure with the *syn* conformation. The use of experimental structures in this kind of calculation is usually adopted due to a large dependence of the magnetic properties on the structural parameters. The same coordination sphere was used for the five metals throughout the calculations.[32] This assumption is a crude approximation, especially in the case of Mn(III) for which a relatively strong Jahn−Teller distortion should be expected, but we are interested more in the broad picture (i.e., whether a relatively strong coupling should be expected or not) than in obtaining precise numerical estimates.

---

(18) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.9; Gaussian, Inc.: Pittsburgh, PA, 1998.

(19) Schaefer, A.; Horn, H.; Ahlrichs, R. *J. Chem. Phys.* **1992**, *97*, 2571−2577.

(20) Schaefer, A.; Huber, C.; Ahlrichs, R. *J. Chem. Phys.* **1994**, *100*, 5829−5835.

(21) Polo, V.; Kraka, E.; Cremer, D. *Theor. Chem. Acc.* **2002**, *107*, 291−303.

(22) Polo, V.; Grafënstein, J.; Kraka, E.; Cremer, D. *Theor. Chem. Acc.* **2003**, *109*, 22−35.

(23) Ruiz, E.; Alvarez, S.; Alemany, P. *Chem. Commun.* **1998**, 2767−2768.

(24) Aquino, M. A. S.; Lee, F. L.; Gabe, E. J.; Bensimon, C.; Greedan, J. E.; Crutchley, R. J. *J. Am. Chem. Soc.* **1992**, *114*, 5130−5140.

(25) Rezvani, A. R.; Bensimon, C.; Cromp, B.; Reber, C.; Greedan, J. E.; Krondatiev, V. V.; Crutchley, R. J. *Inorg. Chem.* **1997**, *36*, 3322−3329.

(26) Robin, M. B.; Day, P. *Adv. Inorg. Chem. Radiochem.* **1967**, *10*, 247−422.

(27) Naklicki, M. L.; White, C. A.; Plante, L. L.; Evans, C. E. B.; Crutchley, R. J. *Inorg. Chem.* **1998**, *37*, 1880−1885.

(28) Evans, C. E. B.; Naklicki, M. L.; Rezvani, A. R.; White, C. A.; Kondraiev, V. V.; Crutchley, R. J. *J. Am. Chem. Soc.* **1998**, *120*, 13096−13103.

(29) Thompson, A. M. W. C.; Gatteschi, D.; McCleverty, J. A.; Navas, J. A.; Rentschler, E.; Ward, M. D. *Inorg. Chem.* **1996**, *35*, 2701−2703.

(30) Tordini, F.; Bencini, A.; Bruschi, M.; De Gioia, L.; Zampella, G.; Fantucci, P. *J. Phys. Chem. A* **2003**, *107*, 1188−1196.

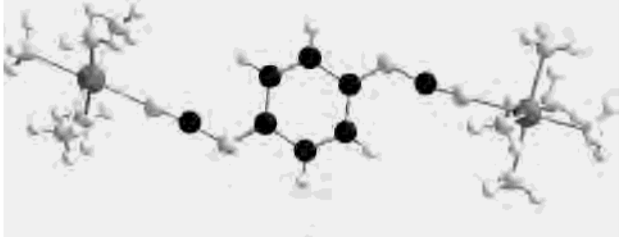
(31) Evans, C. E. B.; Yap, G. P. A.; Crutchley, R. J. *Inorg. Chem.* **1998**, *37*, 6161−6167.

(32) The following structural parameters were used for the model calculations: M−N(NH_3) = 2.10 Å; M−N(dicyd) = 2.08 Å; N−H = 1.0 Å.

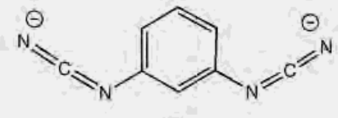
Table 1. Calculated Exchange Coupling Constants for $[(NH_3)_5M(\mu\text{-dicyd})M(NH_3)_5]^{n+}$ with the *para* Bridging Ligand **1** and with the *meta* Isomer **3**

	e^- config	*para*	*meta*
Cr(III)	t_{2g}^3	−161.3	+62.1
Mn(II)	$t_{2g}^3e_g^2$	−0.8	-0.001
Mn(III)	$t_{2g}^3e_g^1$	−177.9	+116.6
Fe(III)	$t_{2g}^3e_g^2$	−289.2	+86.5
Ni(II)	$t_{2g}^6e_g^2$	+0.1	+0.14

The calculated exchange coupling constants for the complexes with the *para* (**1**) and *meta* (**3**) isomers of the dicyd ligand are presented in Table 1. Dramatic changes in the predicted magnetic behavior result depending on the metal ion and the bridging ligand chosen. Hence, we find strong antiferromagnetic coupling for the trivalent metals with the *para* bridge, strong ferromagnetic coupling for the same ions with the *meta* bridge, but practically uncoupled complexes for the divalent metal ions. Probably the most relevant result is the existence of a strong ferromagnetic coupling between trivalent metal ions that are 13.1 Å apart.

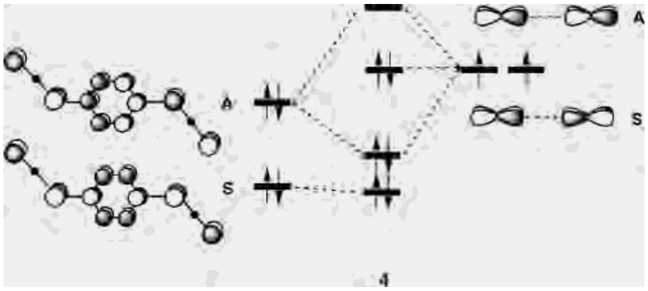


2



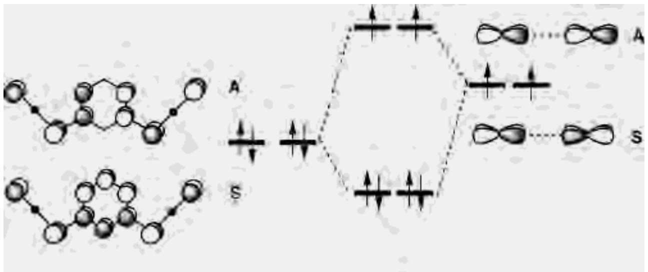
3

The strong antiferromagnetic coupling found for Cr(III) with the *para* bridging ligand can be ascribed mostly to a π-type orbital interaction between one of the d orbitals of t_{2g} character (assuming octahedral symmetry) from each metal atom and the π orbitals of the dicyd ligand, according to the analysis of the Kohn−Sham orbitals,[33] and schematically depicted in **4**. In the absence of the bridging ligands, the symmetric (S) and antisymmetric (A) combinations of those d orbitals at a long distance are degenerate. The A combination interacts with the ligand orbital of the same symmetry and is destabilized, whereas the S combination presents a worse energy match with a low-lying ligand orbital of the same symmetry, thus producing a weak interaction. As a result, a significant gap between the two d orbitals results and the spin-paired (antiferromagnetic) configuration shown is more stable than that with one electron in the higher A orbital and parallel spins (ferromagnetic), according with the Hay−Thibeault−Hoffmann model.[34] The reasons for the relative energies of the ligand S and A orbitals as shown in **4** are given as Supporting Information for the interested reader.



4

In the *meta* complexes of trivalent metals, the orbital interaction is substantially different (**5**), since the S and A π orbitals of the ligand that interact with the well oriented t_{2g} metal orbital are degenerate, thus destabilizing by roughly the same amount the S and A combinations of those d orbitals which remain nearly degenerate. Near degeneracy no doubt favors the ferromagnetic situation, and the fact that the two orbitals are strongly delocalized results in a large exchange integral, hence the large positive values of J found.[34]



5

A study of the Kohn−Sham orbitals for the calculated compounds shows that mixing of the ligand π and metal t_{2g} orbitals is severely diminished when the oxidation state of the metal changes from +3 to +2. This is due to the decreased effective nuclear charge that makes the d orbitals higher in energy and poorer acceptors toward the ligand π orbitals. The decreased mixing accounts for a much smaller energy gap between A and S orbitals in the *para* isomers while, at the same time, results in a much smaller overlap density that is reflected in a smaller exchange integral and also a poorer ferromagnetic coupling in the case of the *meta* isomer. This fact can be easily verified by analyzing the spin population of the isoelectronic d^5 Mn(II) and Fe(III) cations. While the spin population of each Mn atom is + 4.70, it is only +3.83 for Fe, stressing the different degree of delocalization of the unpaired electrons through the bridging ligand. Similarly strong delocalization can also be found for the other trivalent metal complexes, the calculated spin populations being +3.30 for the d^4 Mn(III) cation and +2.60 for the d^3 Cr(III) ion.

The calculated spin density distribution for the ferromagnetic state of the Cr(III) complex with *meta*-dicyd as bridging ligand (Figure 1) nicely reflects the combination of spin delocalization and spin polarization mechanisms.[35] The spin polarization is responsible for the alternation of atoms with positive and negative spin densities, whereas the spin

---

(33) Koch, W.; Holthausen, M. C. *A Chemist's Guide to Density Functional Theory*; Wiley-VCH Verlag: Weinheim, 2000.

(34) Hay, P. J.; Thibeault, J. C.; Hoffmann, R. *J. Am. Chem. Soc.* **1975**, *97*, 4884−4899.

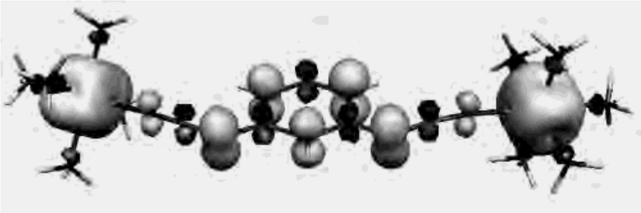


Figure 1. Spin population plot of the high spin solution corresponding to the Cr(III) complex with the 1,3-dicyd ligand (clear and dark regions indicate positive and negative spin populations, respectively).

Table 2. Calculated Exchange Coupling Constants (in cm^{-1}) for $[(NH_3)_5Cr(\mu\text{-dicyd})Cr(NH_3)_5]^{4+}$ Complexes with *para* and *meta* Bridging Ligands with Different Substituents

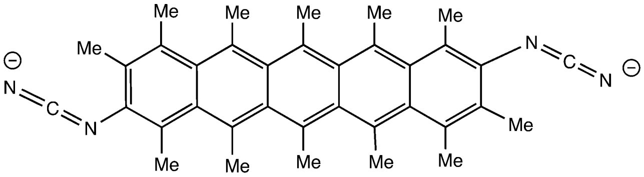
	para	*meta*
dicyd	−161.3	+62.1
Me_4-dicyd	−222.7	+62.3
Cl_4-dicyd	−88.9	+24.0
$(NH_2)_4$-dicyd		+82.7

delocalization can be appreciated by the positive sign of the spin density at the coordinated nitrogen atoms of the dicyd ligand and is responsible for the larger positive atomic densities compared to the negative ones. It is noteworthy that spin polarization affects only the π but not the σ system, which is practically unpolarized. The nitrogen atoms of the terminal NH_3 ligands present negative spin density due to spin polarization, since no delocalization of the unpaired t_{2g} electrons can occur toward those σ donor ligands. The other two complexes of trivalent metal ions studied show almost the same spin population distribution through the bridging ligand, and only small differences at the nitrogen donor atoms are observed, attributable to a larger unpaired electron delocalization when these are in the e_g orbitals, as is the case for Mn(III) and Fe(III).

Given the crucial role of the phenyl ring in the long distance coupling, it is worth exploring the possibility of modulating the interaction via substitution at the aromatic ring. For that purpose we have calculated the coupling constants of Cr(III) complexes with substituted dicyd ligands, using methyl or amino as electron donor and chloro as an electron withdrawing substituent.

The results (Table 2) show that the presence of the donor methyl substituents enhances the exchange coupling, whereas electron withdrawing substituents make it weaker. The effect is smaller for the *meta* isomers, yet a significant enhancement of the ferromagnetic coupling is achieved by introducing amino substituents. These results clearly demonstrate that the exchange coupling constant can be fine-tuned by the appropriate choice of substituents at the bridging ligand.

How far apart can we take the two metal ions without a significant loss of exchange coupling interaction? In order to answer this question, we performed calculations on the very long hypothetical ligand indicated in **6**. The value of J obtained for the Cr(III) complex with this briding ligand, -337.4 cm^{-1}, is still surprisingly high. The existence of a possible artifact in the calculation has been checked by repeating the calculation without the three central aromatic rings (and saturating the two remaining rings with hydrogen atoms), whereupon a negligible coupling was found. Thus, we can confidently predict a very strong coupling for such complex with the two metal atoms at a remarkably long distance of 25.3 Å.



6

In conclusion, complexes of trivalent first row transition metal ions with $t_{2g}{}^n$ electron configurations and dicyd-type bridging ligands constitute interesting synthetic goals for obtaining strong exchange coupling of paramagnetic ions at very long distance. In these systems it is possible to control the strength of the exchange interaction from relatively strong ferromagnetic to antiferromagnetic, and they may also constitute excellent building blocks for a wide variety of structures from simple dinuclear complexes to tridimensional networks as constructed with the related dicyanamide ligands.

Acknowledgment. Financial support came from Ministerio de Ciencia y Tecnología through Project DGI BQU2002-04033-C02-01 and from Comissió Interdepartamental de Ciència i Tecnologia (CIRIT) through Grant 2001SGR-0044. The computing resources at CESCA and CEPBA were generously made available through grants from CIRIT and Universitat de Barcelona.

Supporting Information Available: Additional description and graphics. This material is available free of charge via the Internet at http://pubs.acs.org.

IC026179R

---

(35) Cano, J.; Ruiz, E.; Alvarez, S.; Verdaguer, M. *Comments Inorg. Chem.* **1998**, *20*, 27−56.