

Magnetic Coupling in End-On Azido-Bridged Transition Metal Complexes: A Density Functional Study

Eliseo Ruiz,* Joan Cano, Santiago Alvarez, and Pere Alemany

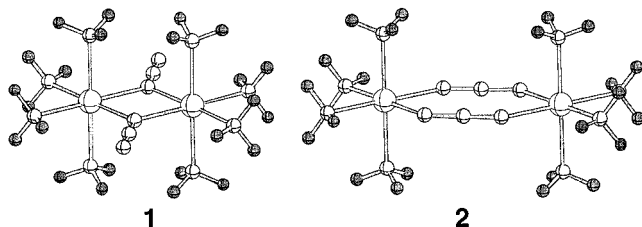
Contribution from the Departament de Química Inorgànica and Departament de Química Física, Facultat de Química, Universitat de Barcelona, Diagonal 647, 08028 Barcelona, Spain

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Abstract: The effect of structural parameters on the exchange coupling constant of the title complexes of Cu(II), Ni(II), and Mn(II) is studied by means of density functional calculations on model compounds. The studied parameters are the bridging M–N–M angle, the M–N bond distance, and the out-of-plane shift of the azido bridge. The model compounds in their most stable geometry, as well as some full molecules in their experimental structures, appear in a high-spin ground state showing ferromagnetic coupling in all cases. The atomic spin density distributions of the model compounds are interpreted as resulting from the interplay between electron delocalization and spin polarization.

1. Introduction

The study of the magnetic properties of materials based on molecular entities has been one of the research topics that has received much attention during the past decades.¹ In this field, the binuclear complexes of transition metals are one of the more extensively studied systems.² The azide anion is a versatile ligand that can bind to transition metal atoms with different coordination modes, thus allowing for the assembly of binuclear complexes with a wide range of magnetic behavior. When the azido group acts as a bridging ligand with end-on coordination (**1**), the resulting binuclear complexes usually show ferromagnetic behavior. In contrast, when it is coordinated in an end-to-end fashion (**2**), antiferromagnetic coupling results.³ The



versatility of this ligand is manifested in the existence of binuclear complexes with one, two, or three bridging azido ligands,⁴ polynuclear complexes with only azido⁵ or with mixed bridges,⁶ as well as of extended⁷ one-dimensional^{8,9} or two-

dimensional¹⁰ networks. Since ferromagnetism in molecular complexes is much less frequent than antiferromagnetism, the ferromagnetic end-on azido-bridged transition metal complexes are specially interesting. An understanding of the factors that favor ferromagnetism in this family of compounds should be useful for the design of novel ferromagnetic materials.

The theoretical study of the magnetic behavior of binuclear transition metal complexes represents a great challenge due to the existence of a manifold of states separated by small energy differences. A qualitative approach that has been employed successfully for the interpretation of magnetostructural correlations is that proposed by Hay, Thibault, and Hoffmann.¹¹ From Hartree–Fock theory, they deduced an approximate formula for the exchange coupling constant J associated to the energy separation between states of different spin multiplicity which, for the case of two centers with one unpaired electron each, can be given by

$$J = 2K_{ab} - \frac{(\epsilon_1 - \epsilon_2)^2}{J_{aa} - J_{ab}} \quad (1)$$

In eq 1, ϵ_1 and ϵ_2 are the energies of the molecular orbitals associated with the unpaired electrons (SOMO's), while K_{ab} , J_{aa} , and J_{ab} are two-electron integrals. The positive term in eq 1 represents a ferromagnetic contribution and the second term an antiferromagnetic contribution, so the nature of the exchange coupling will be ferro- or antiferromagnetic depending on the relative weight of the two terms. The main application of eq 1 so far consists of assuming that the two-electron terms are approximately constant for compounds with the same metal atoms and bridging ligand, which leads to a direct relationship between the coupling constant J and the energy gap between the two SOMO's. Among the limitations of such model, it is clear that one cannot account for differences between strongly ferromagnetic systems (i.e., when the last term in eq 1 is close to zero). An advantage of such approximation is that the

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variations of the orbital gap with changes in structural parameters can be reasonably estimated through semiempirical calculations, the only ones that were affordable for binuclear complexes a few years ago and, still today, much more affordable than *ab initio* calculations.

More precise theoretical estimates of the exchange coupling constant can be obtained using *ab initio* methods.^{12–15} The main drawback of these methods is that, even with the spectacular advances in computational chemistry, they are practically limited to systems with a relatively small number of atoms. Therefore, an important degree of modelization is required, whose effects on the calculated parameters is still not well understood. Recently, we have explored a third way, consisting in the use of hybrid density functional methods (DFT)¹⁶ combined with the broken-symmetry approach proposed by Noodleman,¹⁷ which has been successfully applied to the study of the magnetic properties of hydroxo-, alkoxo-,^{18,19} and oxalato-bridged²⁰ Cu(II) binuclear complexes. Given the ability of density functional methods to handle large systems, such approach allows the calculation of the exchange coupling constants for the complete structures with a good degree of accuracy. On the other hand, a large number of such DFT calculations can also be performed for reasonable model compounds at different molecular geometries, thus allowing for a semiquantitative study of the magnetostructural correlations. Also changes in substituents or counterions can be easily carried out, thus allowing for the evaluation of the effects of chemical substitutions on the magnetic behavior.

In the present paper, we report our DFT results on end-on azido-bridged binuclear complexes of Cu(II), Ni(II), and Mn(II). The two main goals of such work are (i) to study the influence of their structural parameters on the magnetic coupling constant and (ii) to verify the applicability of such methodology to systems with more than one unpaired electron per metal center, since our previous studies focused only on Cu(II) complexes.

2. Computational Details

The exchange coupling constant J for the azido-bridged binuclear complexes has been estimated by calculating the energy difference between the high-spin (HS) state and the broken-symmetry singlet (BS) solution (assuming the spin Hamiltonian is defined as $H = -JS_1S_2$), according to the following expression:

$$J = 2 \frac{E_{\text{BS}} - E_{\text{HS}}}{S(S+1)} \quad (2)$$

where S corresponds to the total spin of the high-spin state. Note that the energy of the broken-symmetry solution is taken as an approximation to that of the singlet state. This procedure avoids the overstabilization of the singlet state²¹ that may result from the double inclusion of some contributions of the electronic correlation when DFT calcula-

tions are used. This procedure is in keeping with the proposal of Perdew, Savin, and co-workers,^{22,23} who suggest that the broken-symmetry singlet determinant is the correct solution of the Kohn–Sham equations for the singlet state. Furthermore, such approach has been shown by us to give values for unmodelized molecules in excellent agreement with experimental data in the case of Cu(II) complexes.^{18–20} The reader must be aware, however, that other authors have employed an expression for the coupling constant originally proposed by Noodleman that mimics a procedure based on a Hartree–Fock determinant,¹⁷ which would yield absolute values of J up to 2 times larger than those reported here. The choice of either approach has no major significance for the qualitative description of the magnetostructural correlations. In particular, the value of a structural parameter for which the crossover from ferro- to antiferromagnetic behavior occurs is independent of the approximation used to estimate the energy of the singlet state from that of the broken-symmetry solution.

All calculations were carried out with the help of the Gaussian 94 program²⁴ using the hybrid B3LYP method proposed by Becke.²⁵ In a previous paper,¹⁸ after evaluating several functionals, we found that the B3LYP method combined with the broken-symmetry approach (indicated as B3LYP-bs in what follows) provides the best results for the calculation of coupling constants. For model structures, we have carried out the calculations with the all-electron double- ζ basis set proposed by Ahlrichs,²⁶ while for the complete structures, we have used a triple- ζ basis set for the metal atom only.²⁷

3. Results and Discussion

3.1. Cu(II) Complexes.

A large number of azido-bridged Cu(II) binuclear complexes have been reported, including end-on double-bridged, as well as end-to-end single- and double-bridged complexes. The end-on double-bridged Cu(II) complexes are all ferromagnetic, and the results of our theoretical study of such compounds will be presented in this section. Although the ferromagnetic behavior of these compounds was formerly attributed to a spin polarization mechanism,²⁸ Kahn et al. have recently measured the polarized neutron diffraction (pnd) spectra of one such compound and determined the distribution of its spin density, showing that the spin at the bridging nitrogen atom has the same sign as that of the metal atoms, thus ruling out the spin polarization model.²⁹ Thompson et al. predicted the possibility of antiferromagnetic behavior for this family of compounds if a large enough Cu–N–Cu angle ($\sim 108.5^\circ$) could be obtained, based on the extrapolation of the

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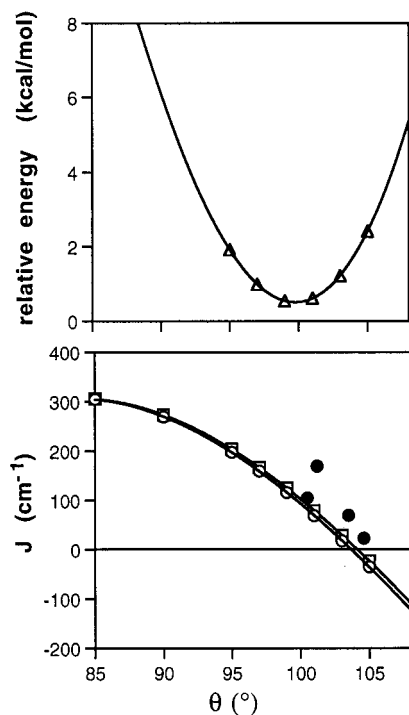
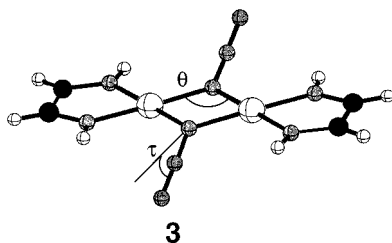


Figure 1. Relative energy of the triplet state (top) and magnetic coupling constants (bottom) for the $[\text{Cu}_2(\mu\text{-N}_3)_2(\text{C}_2\text{N}_2\text{H}_4)_2]^{2+}$ model complex **3** as a function of the bridging angle θ with $\tau = 0^\circ$ (empty circles) and 15° (empty squares). The black circles correspond to experimental values.

magnetostructural correlation found for the end-on μ -azido complexes containing two different bridging ligands.³⁰

We have performed calculations using the model structure³¹ **3** with different values of the Cu–N–Cu angle (θ) and the out-



of-plane deviation of the azido group (τ). The minimum energy has been found for $\theta \approx 100^\circ$, in excellent agreement with the experimental values ($96^\circ < \theta < 104^\circ$)^{30,32–44} that are predicted to be within 2 kcal/mol of the minimum for the triplet state (Figure 1, top). The value of the calculated coupling constant

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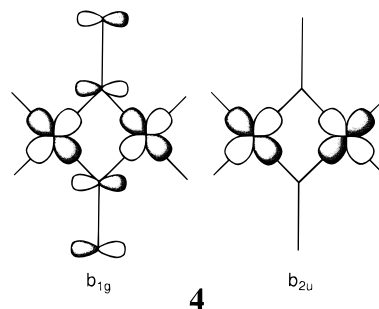
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changes with θ (Figure 1, bottom) in a way similar to that experimentally found by Hatfield and Hodgson⁴⁵ for the hydroxo-bridged complexes: the ferromagnetic coupling decreases from a maximum at about $\theta = 85^\circ$ upon increasing θ , eventually reaching an antiferromagnetic regime for $\theta \geq 104^\circ$. It is interesting to note the large value of the crossover angle compared to that found for the hydroxo-bridged compounds (98°). In the case of the hydroxo-bridged complexes, it was found that the exchange coupling is strongly dependent on the out-of-plane shift of the hydrogen atom (measured by the angle τ , **3**).¹⁸ For the azido-bridged compounds, J has been calculated at two fixed values of τ (Figure 1, bottom), but the results are seen to be practically independent of τ . Notice that the least-squares curves for $J(\theta)$ are in good agreement with the values determined from magnetic susceptibility measurements (see Table 1).

One can reasonably question about the reasons for the dependence of the coupling constant on the θ angle. Since the simple explanation originally proposed by Hay, Thibault, and Hoffmann¹¹ (eq 1) associates the variations in J with changes in the energies of the two SOMO's (ϵ_1 and ϵ_2), we have represented (Figure 2) J as a function of $(\epsilon_1 - \epsilon_2)^2$. Two clear conclusions can be drawn from such plot. On one hand, a clear correlation between the gap and J is found, indicating that the smaller the gap is, the more is a ferromagnetic coupling favored. On the other hand, the relationship between J and the gap is not strictly linear, as would correspond to the expression in eq 1, but deviation from linearity occurs only at those angles that correspond to high-energy structures.

Since the variations of the exchange coupling with the molecular geometry can be associated to the changes in the energies of the SOMO's, we briefly analyze here the nature of these orbitals. The two Kohn–Sham SOMO's of our model calculations are schematically represented in **4**. The b_{1g} orbital



is markedly Cu–N antibonding and is strongly destabilized upon increasing θ , as a result of an enhanced metal–nitrogen overlap. In contrast, the b_{2u} orbital has nonbonding Cu–N character and its energy is practically insensitive to changes in θ . The net result is that the gap increases, hence J decreases with θ . The negligible influence of the out-of-plane shift of the azido group on the coupling constant is also consistent with such orbital picture. The π character of the azide orbital participating in b_{1g} (**4**) makes its overlap with the metal d orbitals independent of τ . This, combined with the Cu–N non bonding nature of the b_{2u} molecular orbital, results in the energy of the two SOMO's being independent of τ .

Our results indicate the possibility of antiferromagnetic end-on azido-bridged Cu(II) binuclear complexes provided the Cu–N–Cu angle is larger than 104° , in agreement with the conclusions of Thompson et al. based on experimental data.³⁰

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Table 1. Structural Parameters (**3**) and Exchange Constants for Bis(μ -azido) Cu(II) and Ni(II) Binuclear Complexes^a

compd ^b	θ	τ	M–N	J_{exptl}	J_{calcd}	ref
[Cu ₂ (μ -N ₃) ₂ (4'-Bupy) ₄](ClO ₄) ₂	100.5	16.7	1.979	+105 ± 20	+191 (+235) ^c	29, 47
[Cu ₂ (μ -N ₃) ₂ (N ₃) ₂ ([24]ane-N ₂ O ₆)]·H ₂ O	101.7; 105.4	6.3; 7.5	2.012	+70 ± 20	+98	32
[Cu ₂ (μ -N ₃) ₂ (N ₃) ₂ (ptdz)]	104.0; 98.5	10.9; 26.8	1.988	+170 ± 2	+50	30
[Cu ₂ (μ -N ₃) ₂ (N ₃) ₂ (bzm) ₂]	104.6	16.6	2.048	+23	+5	48
[Ni ₂ (μ -N ₃) ₂ (232-N ₄) ₂](ClO ₄) ₂	103.8	20.1	2.080	+33.8	+68	56

^a The calculated exchange constants have been calculated for the complete structure using the B3LYP-bs method (see the Computational Details). All angles are in degrees, distances in Å, and J in cm⁻¹. ^b bzm = bis(2-benzimidazolyl)propane); ptdz = 2,5-bis((pyridylmethyl)thio)thiadiazole). ^c The value in parentheses has been calculated with the neutron diffraction structural data.²⁹

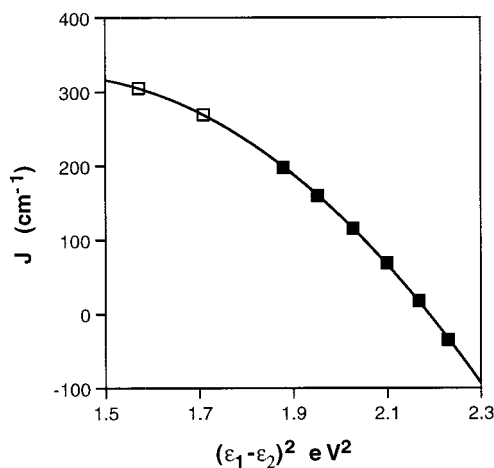


Figure 2. Calculated coupling constant for [Cu₂(μ -N₃)₂(C₂N₂H₄)₂]²⁺ as a function of the square of the gap between the two SOMO's. The black squares correspond to the θ values for which the calculated energy is at most 3 kcal/mol above the minimum.

However, such geometry requires a too small N–Cu–N bond angle (75°), and so far, the largest θ angle found in an end-on azido bridged Cu compound, as assessed by a structural database search,⁴⁶ is that in the compound reported by Reedijk and co-workers, for which a very weak ferromagnetic coupling has been found (Table 1).

A third structural parameter whose influence on the exchange coupling has been analyzed in this work is the Cu–N distance. The calculations were performed using the same model as in the previous case (**3**), and the results are represented in Figure 3. A clear dependence of the exchange coupling constant on the Cu–N distance has been found, with the ferromagnetic coupling decreasing as the Cu–N distance increases, eventually becoming antiferromagnetic at distances larger than 2.05 Å. The experimental results are in excellent agreement with the calculated J values despite the simplifications introduced in the model structure. Furthermore, it is to be noted that the experimental structures present Cu–N distances close to that predicted to have the minimum energy, and within 3 kcal/mol of the minimum.

To evaluate the ability of the present methodology to provide quantitative estimates of the exchange coupling constants, we have performed calculations for several complete molecules including even the counterions. The results are presented in Table 1. For all cases, a triplet ground state has been found, in good agreement with their experimental behavior. The quantitative agreement between the calculated and experimental values of the coupling constants varies from very good to poor, although one must keep in mind that the experimental values for ferromagnetic systems usually have a large uncertainty associated to the fitting of the magnetic susceptibility data. Nevertheless, the dependence of the coupling constant on the

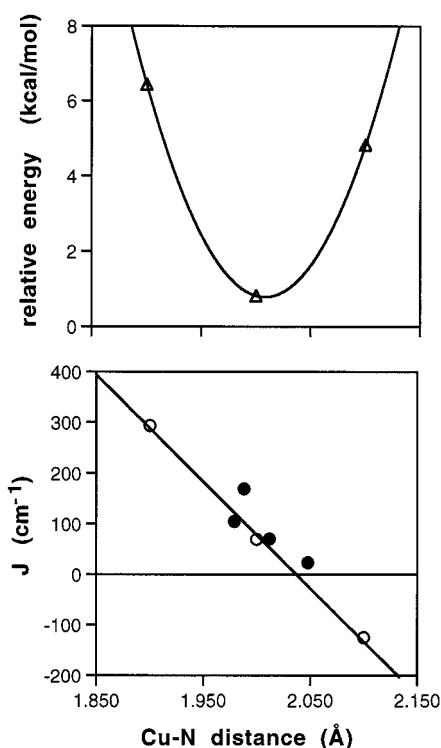


Figure 3. Relative energy of the triplet state (top) and calculated J value (bottom) as a function of the Cu–N distance for the [Cu₂(μ -N₃)₂(C₂N₂H₄)₂]²⁺ model **3** with $\theta = 101^\circ$ (empty circles). The black circles correspond to experimental values.

Table 2. Atomic Spin Densities Obtained from Experimental pnd Data and Calculated for a Model Molecule with a BP Functional,²⁰ Compared to the Values Calculated in the Present Work for the Complete Structure with the B3LYP Method (Mulliken Population Analysis) for [Cu₂(μ -N₃)₂(4'-Bupy)₄](ClO₄)₂

	exptl (pnd) ²⁸	BP ²⁸	B3LYP
Cu	+0.783	+0.425	+0.60
N1	+0.069	+0.167	+0.14
N2	-0.016	-0.005	-0.04
N3	+0.057	+0.122	+0.12
N _{term}	+0.067, +0.049	+0.129, +0.120	+0.09, +0.09

angle θ is clearly illustrated by those symmetrically bridged complexes, which show the strongest ($J_{\text{calc}} = +191$ cm⁻¹) and weakest ($J_{\text{calc}} = +5$ cm⁻¹) ferromagnetic coupling with the smallest and largest angle, respectively (Table 1).

In addition to the exchange coupling constant, it is interesting to study the spin density distribution in such compounds. For one of them [Cu₂(μ -N₃)₂(4'-Bupy)₄](ClO₄)₂ (4'-Bupy = *p*-*tert*-butylpyridine), Kahn et al. have recently determined the spin density maps from polarized neutron diffraction studies.²⁹ The atomic spin densities obtained from such measurements are presented in Table 2, together with the values calculated in the present study for the triplet state. The theoretical results apparently show a tendency to overemphasize the spin delo-

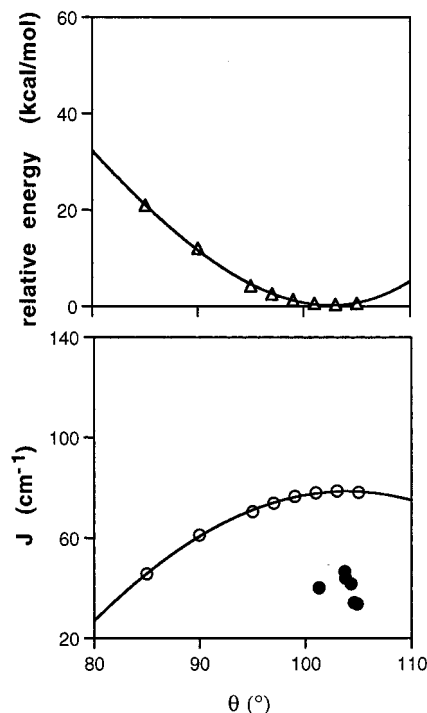


Figure 4. Relative energy of the quintet state (top) and exchange coupling constant (bottom) for the $[\text{Ni}_2(\mu\text{-N}_3)_2(\text{NH}_3)_8]^{2+}$ model 1 as a function of the bridging angle θ (empty circles). The black circles correspond to the experimental values.

calization, thus giving smaller spin densities at the copper atom, although the B3LYP method used here gives a slightly better agreement with experiment than the BP one reported by Kahn et al. The use of the “atoms in molecules” analysis proposed by Bader⁴⁹ in our model calculations results in a higher spin density (+0.66 electrons) at the copper atom, still smaller than the experimentally determined value. The spin densities at the bridging (N1) and terminal (N_t) nitrogen atoms have the same sign as in the copper atoms, both from experiment and from calculations, indicating that spin delocalization toward the donor atoms predominates over the polarization mechanism for this system.⁵⁰ The sign alternation of the spin density at the N2 and N3 atoms of the azido bridge is consistent with spin polarization by the bridging nitrogen atoms. Again, the numerical differences between the experimental and calculated values are probably due to the calculations overestimating the delocalization of the unpaired electrons.

3.2. Bis- and Tris(μ -azido) Ni(II) Complexes. For the bis-(μ -azido) Ni(II) complexes we have first analyzed the influence of the structural parameters on the exchange coupling constant. The calculated J is seen to vary with θ (Figure 4) in a different way to that of the Cu(II) model complex discussed above. The interaction is predicted to be ferromagnetic for all the range of θ angles explored, with J increasing upon increasing θ , yielding a maximum at $\theta \approx 104^\circ$. In this case, the strongest possible

ferromagnetic coupling coincides with the most stable geometry and with the structure shown by the experimentally studied compounds. The available structures show a narrow range of θ values, and the experimental J values also vary little^{51–57} as predicted by Figure 4. For all of them a quintet ground state has been deduced from the magnetic susceptibility data, in good agreement with our calculations. The predicted dependence of the exchange coupling on θ is in good agreement with the results obtained by Castell et al. using the multiconfigurational DDCI2 method,^{12,58} and the preparation of new compounds with quite different bond angles is highly desirable to check the existence of the theoretically predicted magnetostructural correlation.

The calculated J values are overestimated by almost a factor of 2 in comparison with the experimental ones. To verify whether the error is attached to the simplifications assumed in our model compound or to the uncertainty of the computational method, we have calculated the exchange constant for the complete structure⁵⁶ of $[\text{Ni}_2(\mu\text{-N}_3)_2(232\text{-N}_4)_2](\text{ClO}_4)_2$ (see Table 1). The calculated value is 68 cm^{-1} , to be compared with an experimental value of $+33.8 \text{ cm}^{-1}$. That difference cannot be associated to a failure of the employed methodology when applied to systems with more than two unpaired electrons since an excellent agreement between calculated and experimental data has been obtained for oxalato-bridged Ni(II) and for heterobinuclear complexes as well.²¹

As discussed above for the Cu(II) complexes, we have also analyzed the influence of the out-of-plane displacement of the azido group. The effect of that structural parameter (not shown in Figure 4) on the exchange coupling is very small. Finally, the influence of the Ni–N distance also has been investigated, and the results (Figure 5) are similar to those reported above for the copper compounds, indicating a poorer ferromagnetic coupling as the bond distance increases. In this case, though, the experimental data does not seem to follow the predicted trend. At best, disregarding the outlier with the longest distance, a similar qualitative trend can be appreciated, but with a much smaller slope, consistent with the overestimation of the calculated J value by a factor of ~ 2 . Notice that the opposite trend was suggested by Christou, based on the experimental data.⁵⁹ However, we have detected that the experimental data reported by different authors had been fitted to different Hamiltonians. Hence, the experimental data presented by us are consistent with the Hamiltonian ($H = -JS_1S_2$) used throughout in this paper.

The variation of the energies of the SOMO's of $d_{x^2-y^2}$ type with θ show a behavior similar to that discussed above for the Cu(II) complexes, with the energy gap increasing with θ . For Ni(II), though, there are two more SOMO's built up from the metal d_z^2 atomic orbitals, whose energy difference remains practically constant with θ . Thus, the Hay–Thibeault–Hoffmann model (eq 2) cannot explain the existence of a maximum in the $J(\theta)$ curve at $\theta \approx 104^\circ$, suggesting that the two-electron terms in this case are sensitive to changes in the molecular structure. Furthermore, no correlation could be found between

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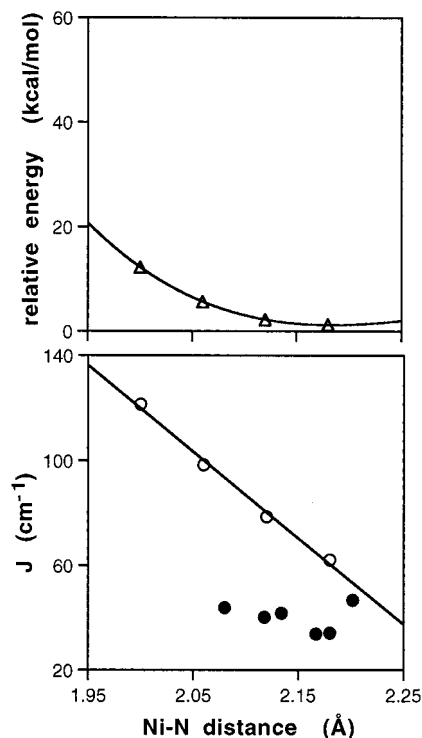


Figure 5. Relative energy of the quintet state (top) and exchange coupling constant (bottom) for the $[\text{Ni}_2(\mu\text{-N}_3)_2(\text{NH}_3)_8]^{2+}$ model **1** as a function of the Ni–N distance with $\theta = 103^\circ$ (empty circles). The black circles correspond to the experimental values.

Table 3. Spin Density Values Obtained from B3LYP Calculations Using the Mulliken Population Analysis for the High-Spin State of Different Model Compounds

atom	Cu(II), 3 $\theta = 101^\circ$	Ni(II), 1 $\theta = 103^\circ$	Ni(II), 5 $\theta = 80^\circ$	Mn(II), 1 $\theta = 105^\circ$
metal	+0.62	+1.68	+1.66	+4.85
N1	+0.14	+0.04	+0.06	−0.05
N2	−0.05	−0.02	−0.02	−0.01
N3	+0.13	+0.11	+0.10	+0.14
N _{term}	+0.09	+0.05	+0.05	+0.01

the calculated J values and the square of the gap between the $d_{x^2-y^2}$ -type SOMO's.

The study of the spin density distribution for the double-bridged Ni(II) complexes (Table 3, second column) indicates two significant differences with the analogous model of copper. First, a proportionally smaller electron delocalization, clearly associated with the formal nonbonding nature of the d_{z^2} -type orbitals. Furthermore, the spin density at the bridging nitrogen atom is still positive, indicating a predominant spin delocalization mechanism, but has a much smaller value than for copper. Two different effects might be at work here: on one hand, the higher energy of the Ni(II) d orbitals should result in a weaker orbital interaction with the ligands and a smaller electron population at the N1 and N_{term} atoms. Besides, a stronger polarization effect is expected for the Ni(II) complexes, since the amount of spin polarization has been found to be roughly proportional to the number of unpaired electrons.⁵⁰

The shape of the calculated $J(\theta)$ curve for the nickel complexes suggests the possibility of obtaining complexes with very weak ferromagnetic or even antiferromagnetic behavior at small θ angles. However, our model calculations (Figure 4, top) for double-bridged complexes indicate that such structures are highly unstable and therefore unlikely to be synthesized. It is in the triple-bridged Ni(II) complexes that such small angles

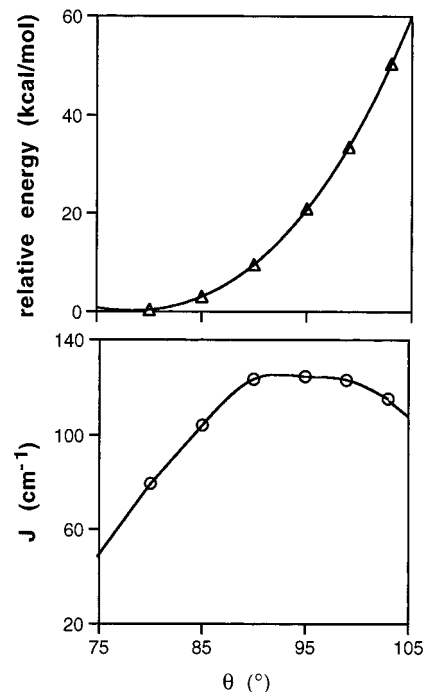
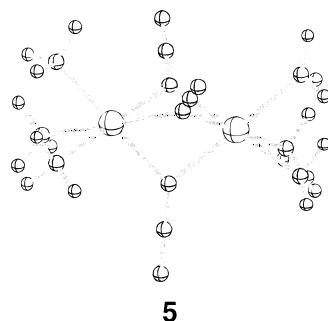


Figure 6. Relative energy of the quintet state (top) and exchange coupling constant (bottom) for the $[\text{Ni}_2(\mu\text{-N}_3)_3(\text{NH}_3)_6]^+$ model **5** as a function of the bridging angle θ .

can be reached. For instance, a binuclear triple-bridged Ni(II) compound has been reported by Beer et al.⁶⁰ with $\theta = 86^\circ$ and $J = +17 \text{ cm}^{-1}$, whereas a chain with alternating end-on and end-to-end azido bridges characterized by Ribas et al.⁶¹ shows an average angle of 84.2° and weak antiferromagnetism ($J = -7 \text{ cm}^{-1}$). Recently, Chaudhuri et al. synthesized a dinuclear complex $[\text{Ni}_2(\mu\text{-N}_3)_3(\text{L})_2]\text{ClO}_4$ ($\text{L} = 1,4,7$ -trimethyl-1,4,7-triazacyclononane)³ with $\theta = 85.9^\circ$ and $J = +61.4 \text{ cm}^{-1}$. We have calculated the exchange coupling constant as a function of θ using model **5** and the results are shown in Figure 6. The



calculated values of J are larger than found for the double-bridge analogues (Figure 4), as expected due to the inclusion of an additional superexchange pathway. As for the double-bridged complexes, we obtain a rapid decay of the ferromagnetic coupling for small values of θ , but even for angles around 80° , a ferromagnetic behavior is predicted in this case, in excellent agreement with the experimental data obtained for the two dinuclear complexes. Castell, using the multiconfigurational DDCI2 method, found a similar dependence with the θ angle but with a smaller values for the exchange coupling constant.⁵⁸ However, the experimental values for the dinuclear complexes

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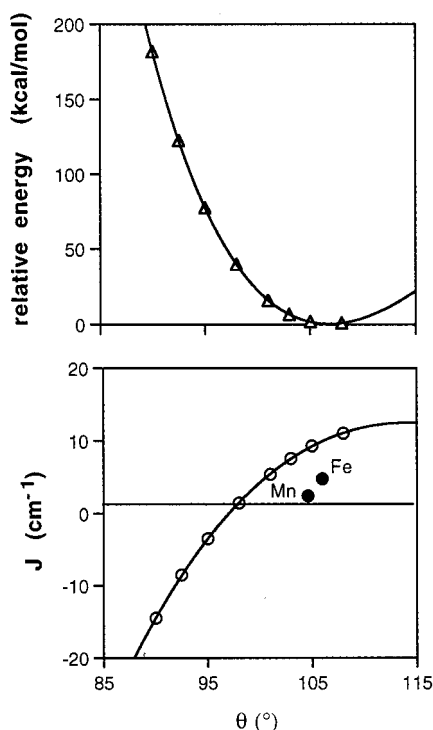


Figure 7. Relative energy of the high-spin state ($S = 5$, top) and exchange coupling constant (bottom) for the $[\text{Mn}_2(\mu\text{-N}_3)_2(\text{NH}_3)_8]^{2+}$ model **1** as a function of the bridging angle θ (empty circles). The black circles correspond to the experimental Fe(III) and Mn(II) complexes described in the literature.

are intermediate between those predicted by our results and the DDCI2 calculations. Thus, these theoretical results agree well with the dependence of the magnetic character on the Ni–N–Ni angle proposed by Ribas et al.⁶¹ An interesting feature of the calculated magnetostructural correlation is the existence of a plateau for the highest values of J , indicating the possibility of obtaining a variety of related compounds with the largest possible ferromagnetic coupling. Unfortunately, a look at the energy of the quintet state as a function of θ (Figure 6, top) shows that such structures are far from the minimum.

3.3. Mn(II) Complexes. There are few examples in the literature of end-on azido-bridged complexes with transition metals other than copper or nickel. We can mention a Co(II) compound reported by Drew et al.⁶² with $\theta = 100.5^\circ$ and $J = +9 \text{ cm}^{-1}$, an Fe(III) complex synthesized by De Munno et al.⁶³ having $\theta = 106^\circ$ and $J = +4.8 \text{ cm}^{-1}$, and a Mn(II) binuclear compound reported by Cortés et al.⁶⁴ with $\theta = 104.6^\circ$ and $J = +2.4 \text{ cm}^{-1}$. To widen the perspective obtained from the above studies on Cu(II) and Ni(II) complexes, we have chosen to study a Mn(II) model compound **1**. The calculated J values for different angles are represented in Figure 7. The general pattern is apparently a parabolic dependence on θ , with a maximum at $\theta = 114^\circ$. Thus, for the manganese complexes, a crossover from ferro- to antiferromagnetism is predicted at $\theta \approx 98^\circ$. Nevertheless, the minimum in energy appears in this case at $\theta = 106^\circ$ and the antiferromagnetic zone appears to be energetically unattainable. Both the preferred θ value and the calculated coupling constants are in excellent agreement with the experimental data for the known Mn(II) and Fe(III) complexes. Of

the five pairs of SOMO's, only those built up from metal $d_{x^2-y^2}$ atomic orbitals (**4**) show a gap that is sensitive to the changes in θ , increasing in an almost linear fashion with θ . The rest of the orbital gaps are practically constant when θ is varied. Furthermore, no correlation has been found between the calculated J values and the energy gaps separating the SOMO's when θ is varied.

The analysis of the spin density distribution for a Mn(II) model complex (Table 3) reveals a larger localization of the unpaired electrons at the metal atom than found for the copper and nickel analogues (compare, e.g., the decreasing spin density at the terminal equatorial donor atoms on going from Cu to Mn). The electron delocalization can be clearly ascribed to the e_g -type orbitals (spin densities of 0.92 and 0.91 for the z^2 and x^2-y^2 orbitals, respectively), while the t_{2g} -type electrons are practically localized at the metal atoms (orbital spin densities of 0.98). Notice that the delocalization decreases from Cu(II) to Ni(II) to Mn(II), a fact that can be associated to the increased energy of the metal d orbitals that makes the metal–nitrogen interaction less covalent. The same argument has been proposed by De Munno et al. to explain the stronger ferromagnetic coupling of the bis(azido) Fe(III) complex in comparison with the Mn(II) complex.⁶³ As a result of the small delocalization for the Mn(II) compound, the spin density at the bridging nitrogen atom is dominated by the polarization mechanism, resulting in a negative spin. The different behavior of the terminal nitrogen atoms is related to the fact that they are polarized by five unpaired electrons of one manganese atom only (equatorial and axial nitrogen atoms have practically the same spin density), whereas the bridging atom is polarized by the 10 unpaired electrons of the two Mn atoms. It is noteworthy that a large positive spin density is found at the terminal nitrogen of the azido group, which is inconsistent with a spin polarization mechanism. A possible explanation is that the topology of the b_{1g} molecular orbital (**4**) provides the same amount of delocalization to N1 and to N3, whereas spin polarization from the small negative density at N1 is almost negligible. Experimental studies of spin density distribution in d^5 compounds appear thus to be interesting in order to advance in our understanding of the interplay between the spin delocalization and spin polarization mechanisms.

It is highly interesting to compare the dependence of the exchange coupling constant on the angle θ for the three end-on bis(azido) model complexes. To facilitate comparison of the results for compounds with different electron configurations, we represent the exchange coupling constant per electron (n^2J) as a function of θ in Figure 8. We have summarized in Table 4 the most relevant parameters of such plots: (i) the θ value for the minimum energy, (ii) the range of values with energies less than 3 kcal/mol above the minimum, (iii) the value of θ for the strongest ferromagnetic coupling, (iv) the θ value for the crossover between ferro- and antiferromagnetic behavior, and (v) the maximum value of J . Let us stress that the crossover angle shown in Table 4 for the Cu complex corresponds to the right branch of the parabola, whereas for the Ni and Mn compounds the crossover of the left branch is indicated, since these correspond to the structures predicted to be most stable. From Figure 8 one can see that the three complexes show the same theoretical behavior, represented by a parabolic dependence of J on θ , with the maxima of the parabola shifted to larger θ values from Cu to Ni to Mn. Since the optimum θ value changes much less than the $J(\theta)$ parabolas, the part of such curves that can be experimentally found (highlighted in Figure 8) correspond to the branch with a negative slope for

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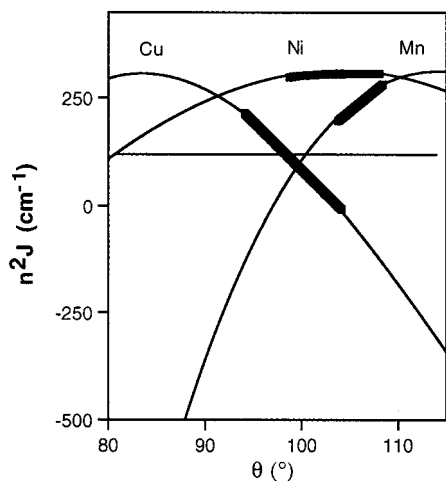


Figure 8. Total exchange constants (n^2J , where n is the number of unpaired electrons per metal atom) for bis(μ -azido) complexes of Cu(II), Ni(II), and Mn(II) as a function of the bridging angle θ . The outlined parts of the curves correspond to those geometries within 3 kcal/mol of the calculated minima.

Table 4. Summary of the Most Relevant Parameters for the Calculated Angular Dependence of J in the Model Complexes (Figures 1, 4, and 6–8)^a

compd	θ_{opt}	θ range	θ_{max}	θ_x	J_{max}
[Cu ₂ (μ -N ₃) ₂ (C ₂ N ₂ H ₄) ₂] ²⁺ (3)	100	93–106	84	104	+307
[Ni ₂ (μ -N ₃) ₂ (NH ₃) ₈] ²⁺ (1)	103	98–109	104	75	+78
[Ni ₂ (μ -N ₃) ₃ (NH ₃) ₆] ⁺ (5)	78	71–85	91–96	72	+125
[Mn ₂ (μ -N ₃) ₂ (NH ₃) ₈] ²⁺ (1)	107	104–109	114	97	+13

^a θ_{opt} is the θ value for the minimum energy, θ -range gives the range of θ values with energies less than 3 kcal/mol above the minimum, θ_{max} is the value of θ for which the strongest ferromagnetic coupling is predicted, θ_x is the θ value for the crossover between ferro- and antiferromagnetic behavior, and J_{max} is the corresponding maximum value of the coupling constant. All angles are in degrees and J in cm^{-1} .

Cu, to that with a positive slope for Mn, and to the region around the maximum for Ni. We are currently investigating the behavior of other families of complexes, to find out whether similar trends can be found when changing the metal atom. Since we have seen that the one-electron contribution to the coupling constant cannot adequately account for the structural dependence of J in the Ni and Mn model complexes, an explanation for such trend should require a detailed study of the two-electron terms and of their dependence on structural parameters and on the nature of the metal atoms.

4. Concluding Remarks

In this contribution we have applied density functional methods to investigate the exchange interaction in end-on azido-bridged transition metal complexes. Our model calculations

indicate that the high-spin state is the ground state for Cu(II), Ni(II), and Mn(II) complexes similar to those characterized by X-ray diffraction which are known to show a ferromagnetic behavior. Calculated exchange coupling constants for several full structures are in fair agreement with the experimental data. There is a clear correlation between the calculated exchange coupling constant and the M–N–M bridging angle, analogous to that found for hydroxo-bridged complexes. The bond angle dependence of the coupling constant can be represented by a parabola, with its maximum appearing at larger angles in the order Cu < Ni < Mn. The out-of-plane displacement of the azido bridge is seen to have a negligible influence on the value of the coupling constant, in contrast to previous findings for the hydroxo and alkoxy bridging ligands. The bond distance between the metal and bridging atoms is also seen to have a strong influence on the coupling constant, with the ferromagnetic coupling diminishing upon increasing such distance. All the experimental structures present structural parameters close to those for which the minimum energy has been calculated.

The analysis of the calculated atomic spin densities for this kind of complexes provides some insight into the mechanisms that determine the spin density distribution throughout the molecule. Our results are in good qualitative agreement with the experimental pnd data recently reported for a copper complex. The delocalization of the unpaired electrons at $d_{x^2-y^2}$ -type orbitals toward the donor atoms decreases along the series Cu > Ni > Mn, while the spin polarization increases in the same direction, due to the increased number of unpaired electrons. As a result, the spin density is positive at the terminal donor atoms and positive at the bridging atoms for Cu and Ni, but small and negative for Mn. An interesting result is that the topology of the b_{1g} molecular orbital appears to be responsible for a large delocalization toward the terminal atom of the bridging azido group, resulting in an almost constant positive spin density for the three metal atoms studied.

The Hay–Thibault–Hoffmann model provides a simple interpretation for the magneto-structural correlation between J and θ for the copper complexes. However, in the cases with more than one unpaired electron per metal atom, as in the Ni(II) and Mn(II) complexes, a more accurate analysis including the two-electron terms is needed.

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