Inorg. Chem. **2009**, *48*, 3139−3144

Inorganic Chemistry
Article

Exchange Interactions in Azido-Bridged Ligand Ni^{II} Complexes: A Theoretical Analysis

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Received December 16, 2008

The exchange-coupling constants in dinuclear 1,1-azidonickel(II) complexes and in one tetranuclear complex have been analyzed by using electronic structure calculations based on density functional theory. The calculated *J* values show a correlation with the Ni−N−Ni angle; however, the available experimental data do not present a correlation between both magnitudes. Hence, new fitting procedures were carried out to obtain a new set of fitted exchange-coupling constants for all of the reported complexes. These new values show a better correlation with the Ni−N−Ni angle close to that found with theoretical methods; however, the calculated values are slightly overrestimated. Experimental and theoretical results indicate that, in the range of the experimental values of the Ni−N−Ni angle (90−105°), the strength of the ferromagnetic coupling increases for larger Ni−N−Ni bond angles.

Introduction

The azido-bridged ligands are one of the most employed in the field of molecular magnetism.[1,2] 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.[3] There are other ligands that also show multiple coordination modes; however, the reason for the azide anion's wide use is very clear: it is almost a unique ligand because when it adopts a 1,1 coordination, the exchange interaction is ferromagnetic. Nature prefers antiferromagnetic couplings that cancel the local spins; hence, in order to have molecules with a large spin, it is crucial to dispose of bridging ligands favoring ferromagnetism. From the experimental point of view, the first studies using the azido ligand with 1,1 coordination (also called end-on) were devoted to dinuclear Cu^{II} complexes, and systems with other cations were rather scarce. During the last years, many new systems of either dinuclear complexes with other cations or polynuclear complexes have been described.[1,2]

During the last years, we have extensively employed electronic structure calculations based on density functional theory (DFT) to study the magnetic properties from dinuclear[4,5] to larger polynuclear complexes.[6−10] From the theoretical point of view, some years ago some of us performed a study centered on the dinuclear 1,1-azidocopper(II) complexes,[11] while some years later, we did a similar study devoted to the dinuclear 1,3-azido-coordinated complexes[12] and also for nonsymmetric complexes.[13] Results for the 1,1-azidocopper(II) complexes showed that the calculated

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Table 1. Structural Data of the Dinuclear Azido-Bridged Ni^{II} Complexes with Only a Double 1,1-Bridging Ligand, Average Ni−N Distances, Ni−N−Ni Bond Angles, and Ni−N−Ni−N Torsion Angles (in Angstroms and Degrees, Respectively) Indicating Also the Refcodes (in Bold Are Those Employed in the DFT Calculations) and Experimental *J* Exchange-Coupling Constants and Zero-Field-Splitting *D* Parameters (in cm^{-1}) and Those Obtained with the New Fitting Procedure

complex[a]	refcodes	Ni−N	Ni−N−Ni	Ni−N−Ni−N	J_{exp}	D_{exp}	J_{new}	ref
$[Ni_2(terpy)_2(\mu_{1,1}N_3)_2(N_3)_2]\cdot H_2O$	**CALWOB**	2.112	101.62	0.0	+45.6	−6.9	+46.3	15
$[Ni_2(terpy)_2(\mu_{1,1}N_3)_3(H_2O)]ClO_4\cdot H_2O$	CALWUH	2.108	100.6, 102.5	−2.08	+27.2	−19.2	+28.3	15
$[Ni_2L_2(\mu_{1,1}\text{-}N_3)_2(N_3)_2]\cdot CH_3OH$	**DAWTUR**	2.164	103.3, 100.3	0.0	+3.82		+2.6	16
$[Ni_2(pbdiim)_4(\mu_{1,1}\text{-}N_3)_2]_2(N_3)\cdot 6H_2O$	FISDUH	2.138	103.0	−0.03	+27.8		+31.9	22
$[Ni_2(L^1)(HL^1)(\mu_{1,1}\text{-}N_3)_2]ClO_4$	GELFAF	2.141	98.0, 98.6	15.80	+10.65	+6.5	+11.0	23
$[Ni_2(L^2)_2(\mu_{1,1}\text{-}N_3)(N_3)(H_2O)]\cdot H_2O$	IXUFEM	2.130	99.4, 102.6	−9.33	+78	+7.3	+52.6	24
$[Ni_2L^3{}_2(\mu_{1,1}\text{-}N_3)_2(N_3)_2]$	JEDHIK	2.140 2.140	100.0, 101.3 97.6	−8.04 0.02	+23.2	+5.27	+23.0	25
$[Ni_2L^4{}_2(\mu_{1,1}\text{-}N_3)_2(N_3)_2]$	JEDHOQ	2.087	99.7	0.0	+47.6	+8.4	+26.4	25
$[Ni_2(232\text{-}tet)_2(\mu_{1,1}N_3)_2(N_3)_2]\cdot 2H_2O$	JEXCIY	2.118	101.3	0.0	+20.1	−12.5	+30.7	26
$[Ni_2(terpy)_2(\mu_{1,1}N_3)_2](PF_6)_2$	NOSJUA	2.180	104.6	0.02	+34.3	+5.9	+44.9	27
$[Ni_2(pepci)_2(\mu_{1,1}N_3)_2(N_3)_2]$	PAKTIE	2.127	101.0, 102.2	0.5	+36.3	−18.8	+69.4	28
$[Ni_2(Me_3[12]N_3)_2(\mu_{1,1}N_3)_2](C1O_4)_2\cdot 2H_2O$	PEJMUM	2.079	103.8	−0.02	+43.9	−13.4	+32.7	29
$[Ni_2(232\text{-}N_4)_2(\mu_{1,1}N_3)_2](C1O_4)_2$	PEJNAT	2.167	104.8	0.0	+33.8	−21.5	+42.4	29
$[Ni_2(en)_2(\mu_{1,1}N_3)_2](C1O_4)_2$	PIMNII	2.133	104.3	0.0	+42.6	+0.17	+23.6	30
$[Ni_2(HL^V)_2(\mu_{1,1}N_3)_2]\cdot 1.5CH_2Cl_2$	**TEQNEJ**	2.121	90.0, 90.8	−0.19	−3.54		−2.47	14
$[Ni_2(HL^V)_2(\mu_{1,1}N_3)_2]\cdot H_2O$	**TEQNIN**	2.144	97.7, 99.6	14.3	+27.3	+5.3	+31.3	14
$[Ni_2(Medpt)_2(\mu_{1,1}N_3)_2(N_3)_2]$	YOMNUJ	2.193	104.0	0.0	+46.7	−5.04	+81.2	31

[a] terpy = 2,2′:6′,2″-terpyridine; L = *N,N*-dimethyl-*N*′-(pyrid-2-ylmethyl)ethylenediamine; pbdiim = 2-(2′-pyridyl)benzo[1,2-*d*:4,5-*d*′]diimidazole]; HL^1 = *N,N*-bis(2-methylpyridyl)-3,5-dimethyl-2-hydroxybenzylamine; L^2 = $Me_2N(CH_2)_2NCHC_6H_3(O^-)(OCH_3)$; L^3 = *N*-(2-pyridylmethyl)-*N*′,*N*′-diethylethylenediamine; L^4 = *N,N*-bis(2-pyridylmethyl)amine; 232-tet = *N,N*′-bis-(3-aminopropaneamine)-1,2-ethanediamine; pepci = *N*′-(2-pyridin-2-ylethyl)pyridine-2-carbaldimine]; $Me_3[12]N_3$ = 2,4,4-trimethyl-1,5,9-triazacyclododec-l-ene; 232-N_4 = *N,N*′-bis(2-aminoethyl)-1,3-propanediamine; en = ethylenediamine; H_2L^V = *N*-(2-pyridyl)methyl)-*N,N*-bis(2′-hydroxy-3′,5′-dimethylbenzyl)amine; Medpt = methylbis-(3-aminopropy1)amine.

exchange-coupling constants for full structure complexes are in excellent agreement with the experimental ones and the reason for the ferromagnetic coupling is related to the degeneracy of the orbitals bearing the unpaired electrons. The main structural parameter that controls such a degeneracy is the Cu−N−Cu bond angle, and a study of the dependence of the exchange-coupling constants with this angle for model complexes with different cations presents a similar parabolic dependence, but the position of the maximum depends on the metal. The second most prolific family of 1,1-azido-bridged complexes is that containing Ni^{II} cations, some of them showing single-molecule behavior. In this paper, we want to perform a theoretical study of the exchange coupling in dinuclear 1,1-azido-bridged Ni^{II} complexes showing only these two bridging ligands and a tetranuclear 1,1-azido-bridged Ni^{II} complex.

Results and Discussion

Exchange Coupling in Dinuclear Ni^{II} Complexes. The calculated *J* values and the main structural parameters for the dinuclear azido-bridged Ni^{II} complexes described in the literature are collected in Table 1; they show octahedral coordination of the Ni^{II} cations with the exception of the PEJNUM complex with pentacoordinate metals. All of the complexes exhibit ferromagnetic behavior with the exception of the TEQNEJ complex, which corresponds to the case of a considerably smaller Ni−N−Ni angle.[14] Taking into account the good correlation between the exchange-coupling constant and the equivalent bond angle for Cu^{II} complexes, we plotted in Figure 1 the dependence between such magnitudes for the Ni^{II} complexes. The analysis of the figure reveals that there is not a good correlation between the *J* value and the Ni−N−Ni angle. Some points seem to follow a common trend, but, in general, there are many cases that fulfill no clear correlation. Thus, we have selected some complexes to calculate the exchange-coupling constant using DFT methods in order to verify whether the experimental fitted *J* value can be reproduced and to analyze the structural parameters that can play a significant role in controlling the magnetic properties in such a family of Ni^{II} complexes.

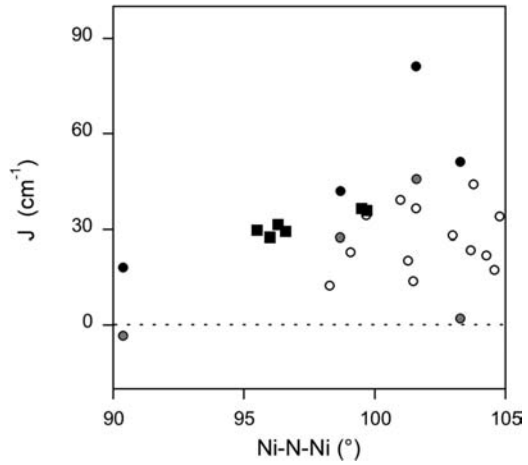

Figure 1. Representation of the dependence of the experimental *J* values for dinuclear azido-bridged Ni^{II} complexes (see Table 1) with average Ni−N−Ni bond angles (white circles filled with gray color for those employed in the calculations) and the calculated *J* values for some of these complexes indicated with black circles and those calculated for the tetranuclear complex as black squares (see the next section).

For such a purpose, we have selected four complexes (see Figure 2). Two cases correspond (CALWOB and TEQNIN)[14,15] to "normal" azido-bridged Ni^{II} complexes with a usual ferromagnetic coupling (+45.6 and +27.3 cm^{-1}), while the DAWTUR complex[16] shows a very small ferromagnetic coupling (+3.81 cm^{-1}) and the TEQNEJ complex (−3.54

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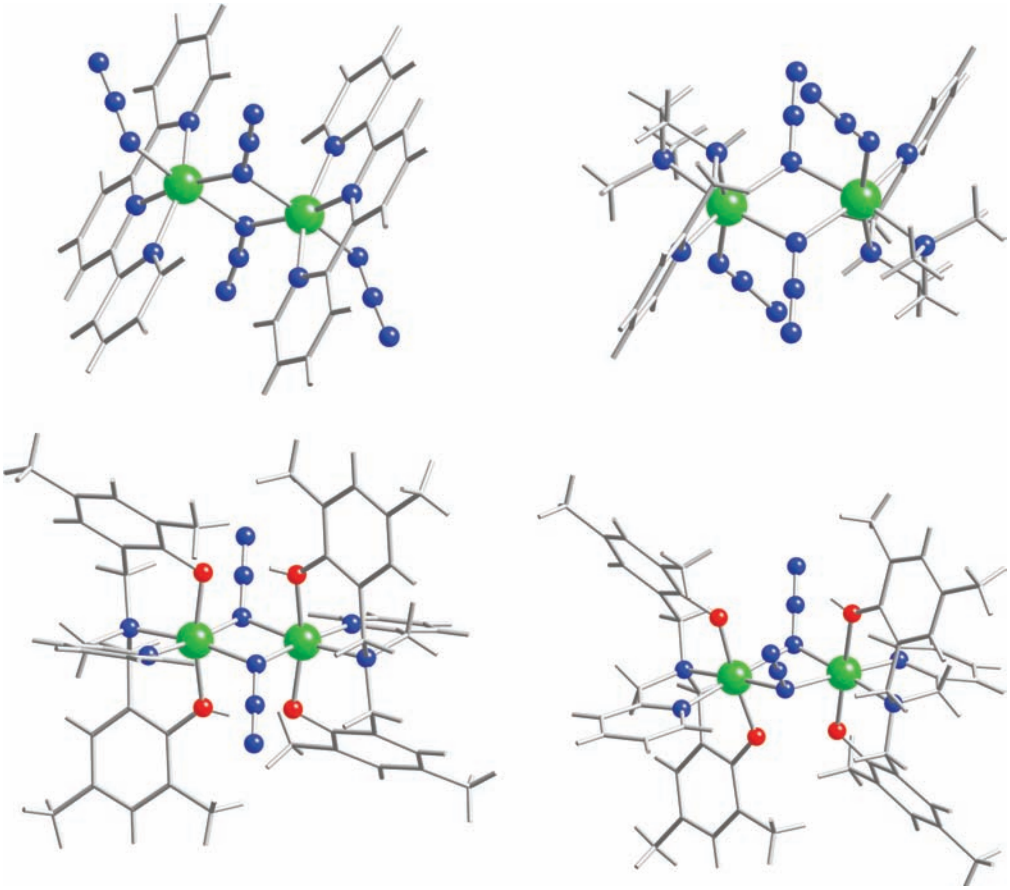

Figure 2. Molecular structure of the studied dinuclear azido-bridged Ni^{II} complexes (CALWOB, DAWTUR, TEQNEJ, and TEQNIN refcodes). Green, blue, and red spheres represent nickel, nitrogen, and oxygen atoms, respectively. Carbon and hydrogen atoms have been indicated for clarity with a wire model.

cm^{-1}),[14] as was previously mentioned, is the unique complex of this family, showing antiferromagnetic coupling and a very small Ni−N−Ni angle. The calculated J values (see the Computational Details section) for the complexes with CALWOB, DAWTUR, TEQNEJ, and TEQNIN refcodes are +80.6, +50.2, +18.3, and +41.9 cm^{-1}, respectively. In all cases, the calculated J values correspond to ferromagnetic couplings, and despite the fact that they follow a similar tendency in the strength of the interactions with the experimental data, the stability of the quintet state is considerably overestimated in comparison with the fitted J values obtained from experimental magnetic susceptibility curves. Such a disagreement between the experimental and calculated J values is surprising taking into account that previously we studied many systems and, in some cases, there were some exceptional cases where some differences between the experimental and calculated values appearred but not for a whole family of complexes.[4,17−19] These discrepancies between calculated and experimental J values for the 1,1-azido-bridged Ni^{II} complexes have been previously pointed out by some of us and other authors.[11,20]

In order to verify the dependence of the calculated J value with the basis set (see the Computational Details section), we performed for the TEQNEJ complex, which shows the largest difference, calculations using a 6-311G basis set and a pseudopotential LANL2DZ basis set, obtaining +16.8 and

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+21.7 cm^{-1} relatively close to the value of +18.3 cm^{-1}. These values confirm that the basis set dependence is rather small and that it is not the source of the discrepancy. Multiconfigurational calculations employing the DDCI2 method using $[Ni(NH_3)_4(N_3)]_2^{2+}$ model complexes corresponding to the JEXCIY complex provide also a relatively too large value (+42.2 cm^{-1}) in comparison with the experimental one (+20.1 cm^{-1}).[21]

The analysis of the fitted *J* values using experimental magnetic susceptibility data reveals the existence of many problems, among others, wrong *J* values due to errors in the Hamiltonian expressions or the inclusion of the zero-field-splitting parameters, which could provide in some cases unrealistic *J* values. The fitted *D* values are very different and do not follow any clear trend (see Table 1). We tried to determine if there is a correlation between them and the octahedral measure of the shape[32,33] for the Ni^{II} cations, but there is not a clear dependence (see Figure S1 in the Supporting Information). *D* values were calculated mainly by means of the Ginsberg equation (see Table S1 in the Supporting Information), and they show a correlation with other terms important at low temperature, for instance, those related with the intermolecular interactions. Unfortunately, more realistic *D* values calculated from magnetization measurements have not been reported for these complexes. Hence, in order to have a proper set of *J* values, we have repeated the fitting procedure for all of the complexes included in Table 1 using the experimental data from high temperature until 70 K in order to avoid the contributions of the zero-field-splitting parameters (see the last column in Table 1). Only in the cases of the DAWTUR and TEQNEJ complexes due to the small *J* value have we included the low-temperature region and, consequently, a *D* parameter in the fit. The *D* parameter employed in such cases corresponds to a local value for the nickel atoms, assuming that both nickel atoms have the same value and neglecting the *E* contribution in order to avoid an overparametrization problem. The obtained *J* values are represented in Figure 2. Now, the new *J* values are closer to following a trend than those reported in the literature, but there are still two or three exceptions. It is important to keep in mind that there are a wide variety of terminal ligands and also difficulties in estimating experimentally the ferromagnetic *J* values that can introduce some discrepancies in the studied complexes.

Analysis of the orbitals bearing the unpaired electrons shows, as expected, the two combinations of $d_{x^2-y^2}$ and d_{z^2} orbitals of the nickel atoms (see Figure 4 for the TEQNEJ complex). We have analyzed the energy gaps between such pairs of orbitals, in order to correlate them with the antiferromagnetic contribution of the exchange-coupling constant through a Hay−Thibeault−Hoffman model.[32] In the case of the TEQNEJ complex, the sum of squares of the two energy gaps is 2.7×10^{-4}, considerably larger than the value of 1.4×10^{-4} obtained for the DAWTUR complex. For the other two complexes, the obtained orbitals are nonsymmetric and the energy values cannot be directly compared. Thus, the larger energy gap for the TEQNEJ complex is in agreement with the antiferromagnetic coupling found experimentally (or, theoretically, the weakest ferromagnetic coupling) for such a system.

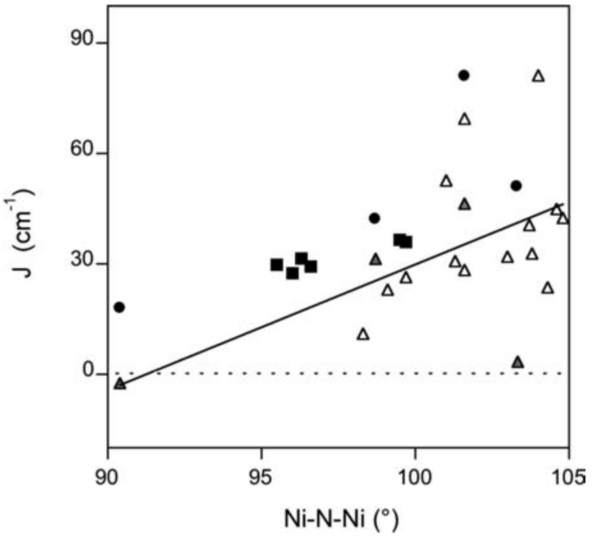

Figure 3. Representation of the dependence of the new fitted experimental *J* values for dinuclear azido-bridged Ni^{II} complexes (see Table 1) with the average Ni−N−Ni bond angle (white triangles filled with gray color for those employed in the calculations) and the calculated *J* values for some of these complexes indicated with black circles and those calculated for the tetranuclear complex as black squares (see the next section).

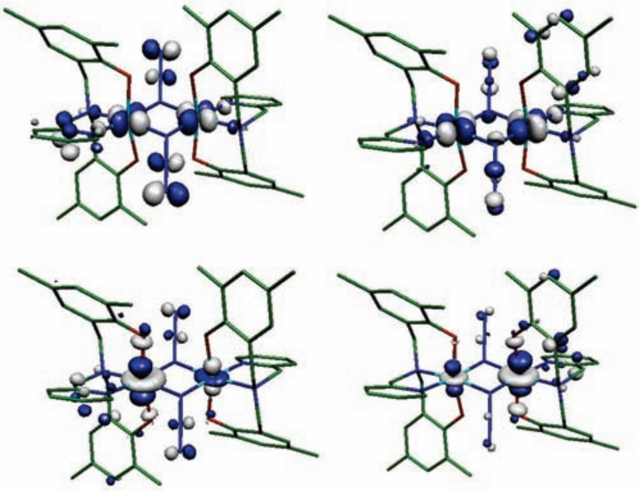

Figure 4. Representation of the orbital bearing the unpaired electrons for the TEQNEJ complex.

Exchange Coupling in a Tetranuclear Cubane-Shaped Ni^{II} Complex. In this section, we studied the magnetic properties of a tetranuclear azido-bridged Ni^{II} complex that adopts a cubane structure (see Figure 5). This complex has low symmetry; thus, the six interactions corresponding to the faces of the cube are different and, consequently, we have calculated six different *J* values, which are collected in Table 2. The six calculated *J* values are relatively similar, and they follow a clear dependence with the Ni−N−Ni angle (see the black squares in Figure 1 or 3). The calculated *J* values for the tetranuclear complex show a correlation with

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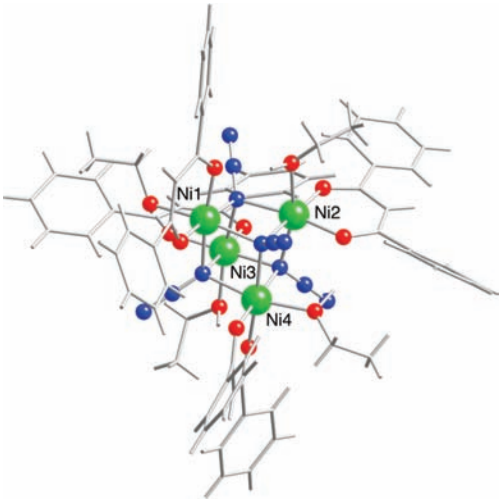

Figure 5. Molecular structure of the cubane-shaped tetranuclear azido-bridged Ni^{II} complex (ZACDAI refcode). Green, blue, and red spheres represent nickel, nitrogen, and oxygen atoms, respectively. Carbon and hydrogen atoms have been indicated for clarity with a wire model.

Table 2. Structural Data of the Tetranuclear Azido-Bridged Ni^{II} Complex (refcode ZACDAI), Average Ni−N Distances, Ni−N−N Bond Angles, and Ni−N−Ni−N Torsion Angles (in Angstroms and Degrees, Respectively) and Calculated *J* Exchange-Coupling Constants (in cm^{-1})

	Ni−N	Ni−N−Ni	Ni−N−Ni−N	J_{ij} (cm^{-1})
J_{12}	2.126	96.1, 96.5	9.44	31.4
J_{13}	2.125	94.8, 96.2	9.93	29.7
J_{14}	2.113	99.1, 100.4	4.30	35.9
J_{23}	2.122	99.3, 99.7	2.77	36.5
J_{24}	2.128	95.6, 97.7	9.75	29.3
J_{34}	2.124	95.9, 96.1	9.66	27.5

the Ni−N−Ni angle similar to that of the values obtained for the dinuclear complexes (see the black circles in Figure 1 or 3 with the exception of the CALWOB complex mentioned above). This trend indicates that a larger Ni−N−Ni angle provides stronger ferromagnetic couplings. However, for the tetranuclear complex, the calculated *J* values (Table 2) overestimate the experimental fitted value of +23.8 cm^{-1}. Similar to dinuclear complexes, the sign is well reproduced but the value is slightly overestimated.

Spin Density in Azido-Bridged Ni^{II} Complexes. The analysis of the spin density for the studied dinuclear and polynuclear azido-bridged Ni^{II} complexes shows similar patterns. The spin density of the Ni^{II} cations is around 1.6e$^-$, indicating a spin delocalization of ca. 0.4e$^-$ on the ligands, basically on the N1 and N3 atoms of the azido ligands together with the coordinated atoms of the terminal ligands. It is worth mentioning that in all cases the spin density of the bridging nitrogen atom is positive, indicating that the spin polarization mechanism employed to justify the existence of ferromagnetic couplings is not valid. The spin polarization appears in the sequence of nitrogen atoms of the azido-bridged ligand; thus, the N2 atom has a negative spin density (see, for instance, Figure 6 for the tetranuclear complex) close to −0.01e$^-$.

Concluding Remarks

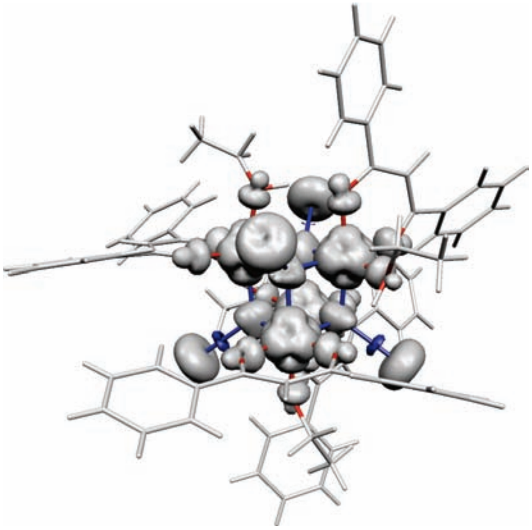

Figure 6. Representation of the spin density corresponding to the ferromagnetically coupled $S = 4$ ground state of the Ni$_4$ complex. The isodensity surface represented corresponds to a value of 0.003e$^-$/bohr^3 (white and blue regions indicate positive and negative spin populations, respectively).

The exchange-coupling constants in dinuclear 1,1-azidonickel(II) complexes and in one tetranuclear complex have been analyzed by using electronic structure calculations based on DFT. For this family of complexes, there is not a clear correlation between the experimentally fitted *J* values and the Ni−N−Ni bond angle. In order to avoid difficulties, anisotropy terms, and intermolecular interactions, we performed a new fitting using the diagonalization of the Hamiltonian but only considering the high-temperature region. The use of these new values improves slightly the correlation with the Ni−N−Ni bond angle but is still far from the agreement found for similar systems.

The calculated *J* values using the B3LYP functional correctly reproduce the ferromagnetic behavior usually found for the dinuclear 1,1-azidonickel(II) complexes, but there is an overestimation of the values. Similar results are found for the studied tetranuclear complex. The origin of such a discrepancy is unclear because the use of other theoretical approaches, such as the spin projection, would even worsen the agreement. It is important to keep in mind also the extreme sensitivity of the experimentally fitted *J* values with the measured magnetic susceptibility data. Experimental and theoretical results indicate that, in the range of experimental values of 90−105°, the strength of the ferromagnetic coupling increases for larger Ni−N−Ni bond angles. The anomalous antiferromagnetic behavior of one the complexes of this family can be explained by the small Ni−N−Ni angle. The analysis of the energies corresponding to the singly occupied molecular orbitals indicated a larger energy difference for this complex and, consequently, a larger antiferromagnetic contribution.

Computational Details

Since a detailed description of the computational strategy used to calculate the exchange-coupling constants in polynuclear complexes is outside the scope of this paper, we will only discuss here

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the most important aspects. A detailed description of the theoretical approach can be found in the literature for dinuclear complexes[4,19] as well as in a review article for polynuclear complexes.[6] For a general polynuclear complex, the Heisenberg Hamiltonian without anisotropic terms can be expressed as

$$\hat{H} = -\sum_{i>j} J_{ij}\hat{S}_i\hat{S}_j \qquad (1)$$

where $\hat{S}_i$ and $\hat{S}_j$ are the spin operators of the paramagnetic centers i and j. The J_{ij} parameters are the exchange-coupling constants for the different pairwise interactions between the paramagnetic metal centers of the molecule. In order to calculate the n different coupling constants J_{ij} present in a polynuclear complex, we need to perform calculations for at least $n + 1$ different spin distributions. By solving the system of n equations obtained from the energy differences, we can obtain the n coupling constants to extract the J values. In the case of dinuclear complexes, the J value is obtained directly from the energy difference of the high spin state, a quintet state for $\mathrm{Ni^{II}}$ complexes, and the broken symmetry $S = 0$ solution divided by a factor of 3. For the tetranuclear complex, seven spin distributions were employed: the high-spin $S = 4$ solution, three cases with $S = 2$ corresponding to the inversion of the Ni2, Ni3, or Ni4 centers, and finally three calculations of a $S = 0$ single determinant with inversion of the {Ni2, Ni4}, {Ni2, Ni3}, and {Ni3, Ni4} pairs.

Recently, we have analyzed the effect of the basis set and the choice of the functional on the accuracy of the determination of the exchange-coupling constants. The calculations performed using the hybrid B3LYP functional,[35] together with the basis sets proposed by Schaefer et al.,[36] provide J values in excellent agreement with the experimental data. We employed a basis set of triple-ζ quality for all atoms. The calculations were performed with the *Gaussian 03* code[37] using initial guess functions generated with the *Jaguar 6.0* code.[38]

Acknowledgment. The research reported here was supported by the Dirección General de Investigación del Ministerio de Educación y Ciencia and Comissió Interdepartamental de Ciència i Tecnologia (CIRIT) through Grants CTQ2008-06670-C02-01 and 2005SGR-00036, respectively. The computing resources were generously made available in the Centre de Supercomputació de Catalunya (CESCA) with a grant provided by Fundació Catalana per a la Recerca (FCR) and Universitat de Barcelona. G.M. is thankful for the HPC program to cover the funds for her stay in Barcelona.

Supporting Information Available: Table with the experimental J and D values indicating the procedure followed for their estimation and the octahedral measure of the shape for all of the $\mathrm{Ni^{II}}$ cations for all of the studied complexes and representation of the dependence of the D values with the octahedral measure of the shape. This material is available free of charge via the Internet at http://pubs.acs.org.

IC802397K

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