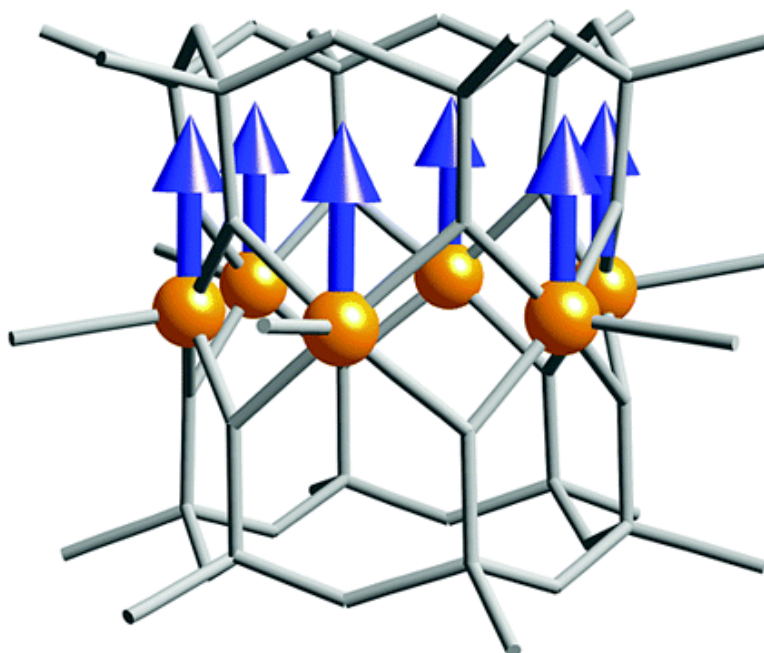


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Theoretical Study of the Magnetic Behavior of Hexanuclear Cu(II) and Ni(II) Polysiloxanolato Complexes

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Abstract: A theoretical density functional study of the exchange coupling in hexanuclear polysiloxanolato-bridged complexes of Cu(II) and Ni(II) is presented. By calculating the energies of three different spin configurations, we can obtain estimates of the first-, second-, and third-neighbor exchange coupling constants. The study has been carried out for the complete structures of the Cu pristine cluster and of the chloroencathrated Ni complex as well as for the hypothetical pristine Ni compound and for magnetically dinuclear analogues M_2Zn_4 ($M = Cu, Ni$).

One of the aspects of current interest in the field of molecular magnetism is the synthesis and study of large clusters with high total spin and marked anisotropy that can result in nanosized molecules that behave as magnets.^{1–3} In this field, theoretical studies can be of great help both for the understanding of the observed behavior of new compounds and for predicting synthetic targets for which interesting properties could be expected. The calculation of the ferro- or antiferromagnetic nature of the exchange coupling of two paramagnetic centers as well as good semiquantitative estimates of the coupling constant is becoming affordable by using density functional theory methods^{4,5} or a difference dedicated configuration interaction⁶ approach. On the other hand, the a priori calculation of the molecular magnetic anisotropy has been achieved recently.⁷ It is therefore timely to explore the possibilities to extend the theoretical studies on exchange coupling from di- to polynuclear complexes.

A suitable case study is provided by the well characterized hexanuclear complexes of Cu⁸ and Ni⁹ with polysiloxanolato

ligands, because of their moderately large size and because the former is ferromagnetic⁸ whereas the latter is antiferromagnetic.⁹ The structures of these two compounds are shown in Figure 1. In brief, the six metal atoms are arranged in a hexagonal ring, linked by bridging siloxanolato groups. At each Cu atom, a fifth coordination position is occupied by a methanol molecule, resulting in a square pyramidal coordination sphere. Similarly, an ethanol molecule is coordinated to each Ni atom in the corresponding compound, the main difference relative to the Cu analogue being the presence of a chloride in the center of the hexagon within 2.8–2.9 Å of the six Ni atoms.

Computational Methodology

The computational strategy adopted in previous theoretical studies on exchange-coupled binuclear complexes⁴ has been adapted to the hexanuclear complexes by using two different approaches.^{10–12} Since no spin-orbit coupling is considered in the present calculations, the magnetic anisotropy needs not be considered. The first approach consisted of evaluating the exchange coupling constant J_{ij} between two paramagnetic metal centers i and j in the hexanuclear molecule by calculating the energy difference between the highest and lowest spin states of a model molecule in which metal atoms are substituted by diamagnetic Zn^{2+} cations in all positions but i and j . A total of 15

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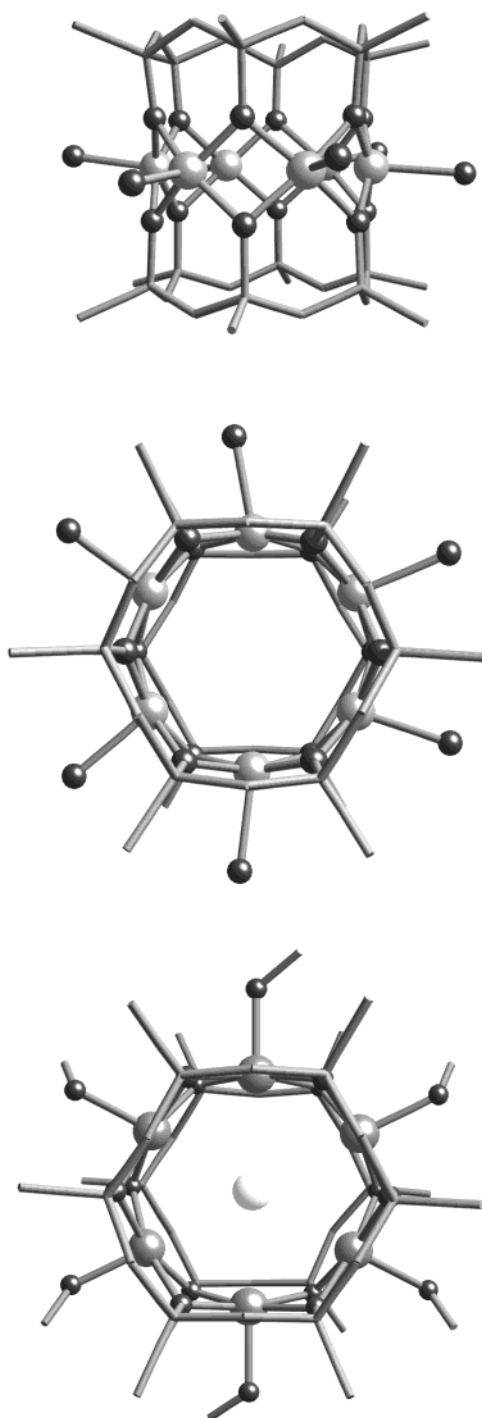
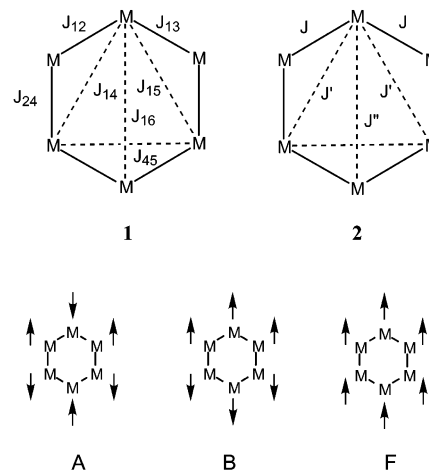


Figure 1. View of the central core of the hexanuclear polysiloxanolato Cu_6 (top and middle) and Ni_6 (bottom) complexes. The phenyl groups of the bridging polysiloxanolato ligands and the substituent of the terminal alcohol ligands are not shown for simplicity.

pairwise coupling constants can in principle be calculated (see sketch 1), but these are reduced by symmetry, yielding only three independent coupling constants for a symmetric hexagon:

$$\begin{aligned} J &= J_{12} = J_{13} = J_{24} \dots; \\ J' &= J_{14} = J_{15} = J_{45} \dots; \\ J'' &= J_{16} = J_{25} = J_{34} \end{aligned} \quad (1)$$

whereas the symmetry is C_3 in the Cu_6 complex and C_2 in the Ni_6 analogue.



For the evaluation of each coupling constant, two separate DFT calculations¹³ are carried out, from which the energies of the highest spin (E_{HS}) and a broken-symmetry singlet configuration (E_{BS}) are obtained as applied for dinuclear complexes,⁵ whereupon the coupling constants are approximately

$$J_{ij} = 2(E_{\text{BS}}^{\text{DFT}} - E_{\text{HS}}^{\text{DFT}}) / S_{\text{HS}}(S_{\text{HS}} + 1) \quad (2)$$

In the second, more rigorous approach, tested by us on tri- and tetranuclear benchmark systems^{14,15} and applied to cubane-shaped tetranuclear copper clusters,¹⁶ we have calculated three different spin configurations of the real hexanuclear molecule: **A** and **B** with $S = 0$, and **F** with $S = 3$ (for Cu^{II}) or $S = 6$ (for Ni^{II}). The only modelisation adopted was to substitute the phenyl rings of the polysiloxanolato ligands by hydrogen atoms. From the calculated relative energies of these spin configurations, one can then extract exchange coupling constants by associating them to energy expressions obtained as a sum of pairwise interactions, as introduced in the Heisenberg Hamiltonian. Given the energy differences between the three states, we can evaluate the exchange coupling constants by adopting either the approximation $J' \approx 0$ (eqs 3) or $J'' \approx 0$ (eqs 4),

$$\begin{aligned} J &= (E_{\text{A}} - E_{\text{B}}) / 4\sigma \\ J'' &= (E_{\text{A}} - E_{\text{F}}) / 3\sigma - 2J \end{aligned} \quad (3)$$

$$\begin{aligned} J &= (E_{\text{A}} - E_{\text{F}}) / 6\sigma \\ J' &= J - (E_{\text{A}} - E_{\text{B}}) / 4\sigma \end{aligned} \quad (4)$$

where $\sigma = 2S_1S_2 + S_1$ (being $S_1 \leq S_2$).

An interesting relationship appears when we assume that $J' \approx J'' \approx 0$, whereupon the energy differences between the two singlets and the ferromagnetic state are in a 3:1 ratio

$$(E_{\text{A}} - E_{\text{F}}) \approx 3(E_{\text{B}} - E_{\text{F}}) \quad (5)$$

The hybrid B3LYP method has been used in all calculations as implemented in Gaussian code,¹² mixing the exact Hartree–Fock exchange with the Becke's expression for the exchange¹⁰ and using the Lee–Yang–Parr correlation functional.¹⁷ We have previously found that, among the most common functionals, the B3LYP method

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Table 1. Exchange Coupling Constants Calculated for the Cu Hexanuclear Compound Using Magnetically Dinuclear Compounds by Means of Diamagnetic Zn²⁺ Substitution (Cu₂Zn₄ Column) and for the Full Hexanuclear Complex Using the Approximations of Eqs 3 and 4, Respectively

	Cu ₂ Zn ₄	Cu ₆ , eq 3	Cu ₆ , eq 4	Cu ₆ , exptl	
				reference 8	this work
<i>J</i>	+38 (av) ^a	+38.1	+37.9	+42	+37.5
<i>J'</i>	-0.3		-0.26	<i>b</i>	-0.62
<i>J''</i>	-1.3	-0.52	-	<i>b</i>	-1.35

^a Average of two first-neighbor interactions: $J_{12} = +33 \text{ cm}^{-1}$ and $J_{13} = +43 \text{ cm}^{-1}$. ^b Assumed to be negligible.

Table 2. Exchange Coupling Constants Calculated for the Ni Hexanuclear Compound Using Magnetically Dinuclear Compounds by Means of Diamagnetic Zn²⁺ Substitution (Ni₂Zn₄Cl column) and for the Full Hexanuclear Complex Using the Approximations of Eqs 3 and 4, Respectively, with or without the Central Chloride Ion

	Ni ₆ , eq 3	Ni ₆ , eq 4	Ni ₂ Zn ₄ Cl ^a	Ni ₆ Cl, eq 3	Ni ₆ Cl, exptl	
					reference 9	this work
<i>J</i>	+3.96	+4.01	+22.8	+25.4	+18.6	+17.8
<i>J'</i>		+0.05	-3.3		-11.8 ^b	-3.9
<i>J''</i>	+0.10		-26.3	-28.1	-11.8 ^b	-22.2

^a For the Ni₂Zn₄Cl case, the values given are the averages of the analogous but nonequivalent coupling constants (*J* is the average of J_1 , J_{13} , and J_{24} ; *J'* is the average of J_{14} , J_{15} , and J_{45}). ^b *J'* and *J''* were assumed to be equal for the fitting procedure.

combined with the broken-symmetry^{18–21} treatment provides the best results for calculating coupling constants,^{4,5} as compared to experimental data. Probably the disagreement between coupling constants obtained using spin projection on the density functional results and experiment is associated with a cancellation of the nondynamic correlation effects, as stressed recently by Polo et al.²² A basis set of triple- ζ quality²³ was used for the Cu and Ni atoms and of double- ζ quality²⁴ for other atoms in all calculations. The adoption of a guess wave function that correctly describes the electronic configuration of each spin state proved to be a crucial step in the calculation of their energies. To that end, we used the program JAGUAR (version 4.1) to prepare the guess wave functions that were then transferred to the GAUSSIAN suite of programs to proceed as in previous works with the simpler binuclear complexes.

A new fitting of the experimental magnetic susceptibility data²⁵ for the two studied complexes has been carried out by a full diagonalization of the Hamiltonian matrix assuming only three coupling constants, as in eq 1, and is shown in Tables 1 and 2. For the Cu₆ complex, other parameters adjusted in the fitting procedure were $g = 2.11$ and a Weiss correction $\theta = -1.04 \text{ cm}^{-1}$ that takes into account intermolecular contacts and zero field splitting effects of the ground state, and an agreement factor of 1.7×10^{-5} was obtained. For Ni₆Cl, $g = 2.316$ and an agreement factor of 2.2×10^{-5} were obtained from the fitting. Theoretical $\chi T(T)$ and $\chi(T)$ curves were obtained with the *J* values calculated for the real complexes (Table 1, second column; Table 2, fourth column), using the *g* values of the presently reported fitting of the experimental data.

Results and Discussion

For the Cu₆ complex, the calculated relative energies for the spin configurations **A**, **B**, and **F** are those indicated in Figure 2

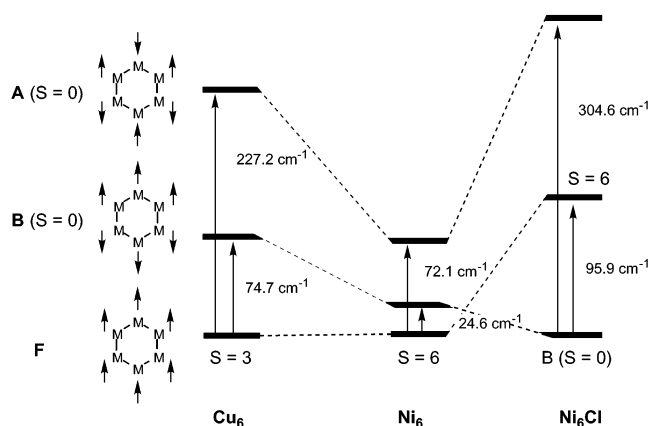


Figure 2. Calculated energies for three different spin configurations of the hexanuclear complexes.

(left). From those energies one can deduce two of the coupling constants (see 2) through either of the approximations given by eqs 3 and 4 (Table 1). The alternative approach of using for calculations hypothetical Cu₂Zn₄ complexes, which are dinuclear from the point of view of magnetism, gives us all the unique coupling constants (see 1) J_{12} , J_{13} , J_{14} , and J_{16} . Since the two first-neighbor coupling constants J_{12} and J_{13} have similar values, we take their average *J'* from here on.

The coupling constants obtained with the different approaches (first three columns in Table 1; see 2 for definitions) consistently give the same qualitative and semiquantitative description of the exchange interactions: first-neighbor interactions are ferromagnetic, with *J* values of about $+38 \text{ cm}^{-1}$, as expected from the Goodenough–Kanamori rules for the bridging Cu–O–Cu angles $91–92^\circ$, and in excellent agreement with the value reported as the best fit to the experimental magnetic susceptibility data ($+42 \text{ cm}^{-1}$).⁸ Second- and third-neighbor interactions are much weaker and just marginally antiferromagnetic in our calculations, thus providing support to the hypothesis adopted for the previous fitting of the experimental data,⁸ namely $J' \approx J'' \approx 0$. The temperature dependence of the magnetic behavior resulting from the theoretical *J* values is plotted in Figure 3 (top) alongside the previously reported experimental data, showing an excellent agreement down to 20 K. At a lower temperature, a somewhat better agreement is obtained (dashed line, extrapolating to $\chi T \approx 3.0$ near 0 K) if intermolecular interactions and zero field splitting are incorporated into the expression of the magnetic susceptibility, as proposed by Cornia et al.⁹ A new fitting of the experimental data guided by the calculated values yields coupling constants (Table 1, last column) consistent with the theoretical results obtained with three different approaches (Table 1, first three columns). Remarkably, the magnetic behavior of this hexanuclear Cu compound can be essentially explained through only first-neighbor interactions.

For the case of the Ni compound, we discuss first the calculations for the so far hypothetical molecule without the chloride guest, abbreviated as Ni₆, and then we will consider the real Ni₆Cl system. In the former case, the calculated energies for the three spin configurations considered are shown in Figure 2 (center). It is seen that the energy ordering is the same as that for the Cu₆ analogue but with smaller energy differences, reflected by the resulting positive coupling constant between nearest neighbors. It is to be noted that both approximations

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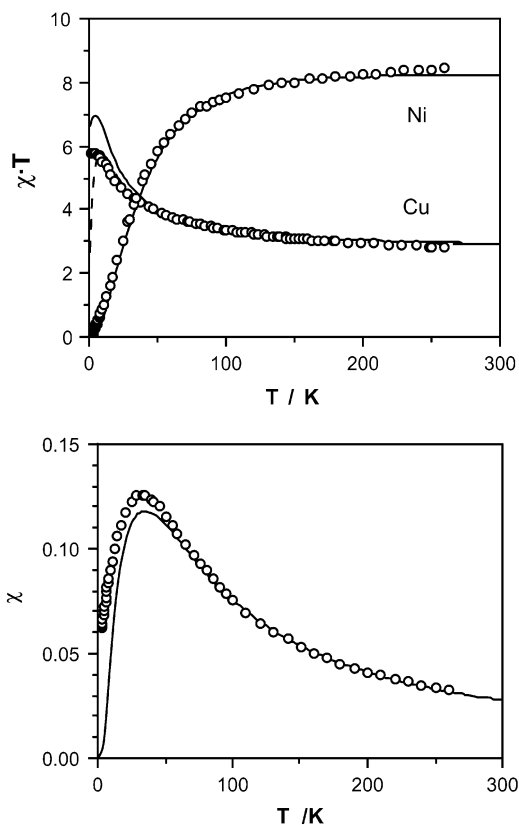


Figure 3. Experimental (circles) $\chi T(T)$ curve for the Cu_6 and Ni_6Cl complexes (top) compared to the curves (continuous lines) obtained with the theoretical J values for Cu_6 (Table 1, second column) and Ni_6Cl (Table 2, fourth column). For the Cu_6 compound, an alternative theoretical curve obtained by including intermolecular interactions and zero field splitting in the expression of the magnetic susceptibility⁹ is also shown (dashed line), deviating from the experimental data only at very low temperatures. The data for Ni are also represented as a $\chi(T)$ curve (bottom) to show the difference between calculated and experimental magnetic susceptibilities at low temperatures.

embedded in eqs 3 and 4 consistently give negligible second- and third-neighbor coupling constants.

The presence of the guest chloride in the center of the hexanuclear ring dramatically affects the energies of the spin configurations considered (Figure 2, right), clearly indicating an antiferromagnetic behavior, as experimentally found.⁹ Such energy ordering scheme translates into the coupling constants of Table 2 (third and fourth columns), significantly ferromagnetic between nearest-neighbors, of the same order of magnitude but antiferromagnetic for the interaction through the linear Ni–Cl–Ni bridge (J''), and rather small for second neighbors (J').

A better idea of how well the calculated coupling constants describe the magnetic behavior of this compound can be obtained by looking at Figure 3, where we show the theoretical $\chi T(T)$ curve together with the previously reported experimental values (top) and the $\chi(T)$ curve (bottom) that is more sensitive to the agreement around the maximum. Therefore, in this case the approximation used for fitting the temperature dependence of the magnetic susceptibility ($J' = J''$) seems to be inappropriate. Using the calculated values as the starting point for a new fitting of the experimental data, we obtain coupling constants (Table 2, last column) that are in excellent agreement with the calculated values for the $\text{Ni}_2\text{Zn}_4\text{Cl}$ and Ni_6Cl clusters. Comparison of the results obtained for the pristine M_6 clusters with those for the Ni_6Cl compound with a chloride guest allows us to conclude that the interaction of the Ni d_{z^2} orbitals through the chloro bridge determines its different behaviors, as previously proposed by Cornia et al.⁹

Concluding Remarks

The theoretical evaluation of exchange coupling constants in the studied hexanuclear complexes, carried out either for the real cluster or for Zn substituted model compounds, yields values which are consistent and in good agreement with experimental data for the case of polysiloxanolato hexanuclear complexes of Cu(II) and Ni(II). The present results indicate that ferromagnetic interactions between first neighbors dominate the magnetic behavior of these compounds in the absence of a central guest anion, whereas the presence of a chloride guest in the Ni(II) compound is responsible for an antiferromagnetic coupling between third-neighbor Ni atoms, thus confirming the explanation proposed earlier for the different behaviors of the Cu and Ni compounds. Calculations such as those presented here can in the future be of help in providing guidelines for the best approximations that can be adopted for fitting the experimental magnetic susceptibility curves to a spin Hamiltonian.

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