

Theoretical study of the electronic properties and exchange coupling in a Ni₄ cubane like single-molecule magnet

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Abstract

Density functional theory (DFT) calculations on the tetranuclear Ni(II) complex [Ni₄(C₅H₁₁O₃)₄(CH₃CN)₄](NO₃)₄ · 1.33NaNO₃, have been made in order to explain the exchange magnetic phenomenon. Two ferromagnetic exchange coupling constants were found ($J_1 = +13.27 \text{ cm}^{-1}$ and $J_2 = +12.86 \text{ cm}^{-1}$) and these values are close to each other and consistent with the structural parameters of the complex.

Keywords: DFT calculations; Ni complex; Cubane like; Spin density

1. Introduction

Many efforts have been made in the last years to obtain new polynuclear transition metal complexes with a large number of unpaired electrons at the metal centres. These systems are expected to present new magnetic properties [1–3]. Complexes which present a slow relaxation of their magnetization are named single-molecule magnets (SMM) [4]. This phenomenon opens up the possibility of information storage at the molecular level and in the field of quantum computing, due to the presence of quantum tunnelling. The energy barrier that controls such processes is $-D \cdot S^2$, where D is the zero-field splitting parameter and S the total spin of the molecule. Thus, the requirements for such systems to have the high barriers needed to use them to store information are a large spin in the ground state and a large negative D parameter. The first reported Ni^{II}-based SMM was [Ni₁₂(chp)₁₂(O₂CMe)₁₂(H₂O)₆(THF)₆] [5]. Another studied family of SMM are nickel compounds showing smaller nuclearity, i.e. tetranuclear complexes with an $S = 4$ ground state [6–8]. These smaller systems are

particularly interesting due to the presence of ferromagnetic coupling and a large anisotropy of the Ni^{II} cations which make them good candidates for SMM. Despite the small nuclearity, such systems should be important if they have a large D value [9]. In the present work we present the theoretical study using methods based on density functional theory (DFT) of a tetranuclear nickel complex with a cubane-like arrangement which shows ferromagnetic coupling, [Ni₄(C₅H₁₁O₃)₄(CH₃CN)₄](NO₃)₄ · 1.33NaNO₃, reported by Moragues-Cánovas et al. [6]. In this compound, each of the monodeprotonated tridentate ligands occupies terminal positions through two hydroxo groups and a bridging position corresponding to a vertex of the Ni₄O₄ cube. The octahedral coordination sphere of each Ni atom is composed of three bridging alkoxo groups, two terminal hydroxo groups and one acetonitrile molecule.

2. Computational details

All the calculations were performed using the crystal structure of the molecule [6]. Single point calculations were performed with the Gaussian03 code [10] using the quadratic convergence approach with the hybrid B3LYP functional [11] and a guess function generated with the

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Jaguar 5.5 code [12]. We have employed a triple- ζ all electron Gaussian basis set for all atoms [13]. The crystal structure does not include eight hydrogen atoms bonded to two of the terminal oxygens of the tripodal ligand. The hydrogen atoms were added to the structure and optimized with MM+ molecular mechanics force field using the TITAN package [14]. The molecule has two different Ni–Ni distances (3.057 and 3.067 Å), and therefore two different exchange coupling constants (J_1 and J_2) are expected. In order to obtain the two different J values, three calculations are needed: a high spin solution ($S = 4$) and two solutions with $S = 0$, the first one with Ni3 and Ni4 showing spin down and the second solution showing Ni2 and Ni4 with spin down. The spin-density plot was performed with Molekel code [15]. The calculated temperature dependence of the magnetic susceptibility and the magnetization versus external field curve at 4 K were obtained with the Magpack package [16] using $g = 2.18$ as reported by Moragues-Cánovas et al. [6]. No anisotropic parameter was used.

3. Results and discussion

We have considered a general spin Hamiltonian that includes two first-neighbour coupling constants (J_1 and J_2).

$$\hat{H} = -J_1[\hat{S}_1\hat{S}_2 + \hat{S}_1\hat{S}_4 + \hat{S}_2\hat{S}_3 + \hat{S}_3\hat{S}_4] - J_2[\hat{S}_1\hat{S}_3 + \hat{S}_2\hat{S}_4], \quad (1)$$

where \hat{S}_i are the spin operators of each paramagnetic Ni^{II} centre (Fig. 1). Therefore, the studied system presents $4J_1$ and $2J_2$. A detailed description of the procedure used to obtain the exchange coupling constants can be found in previous work of Ruiz et al. [17,18]. The general expression without spin projection to evaluate the J value for the interaction between two centres with more than one unpaired electron is

$$J = \frac{(E_{LS} - E_{HS})}{2S_1S_2 + S_2}, \quad (2)$$

where E_{LS} is the total energy for the low spin solution and E_{HS} is the total energy for the high spin solution,

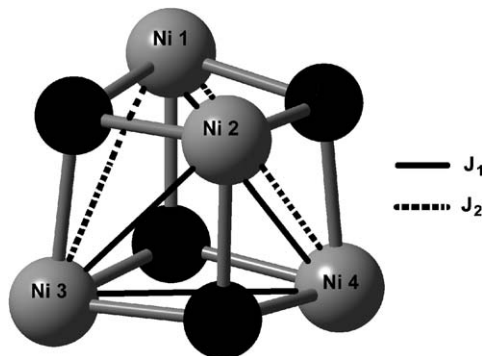


Fig. 1. Topology of the exchange coupling constants in the Ni₄O₄ cube. Ni atoms in grey, μ₃-O atoms in black.

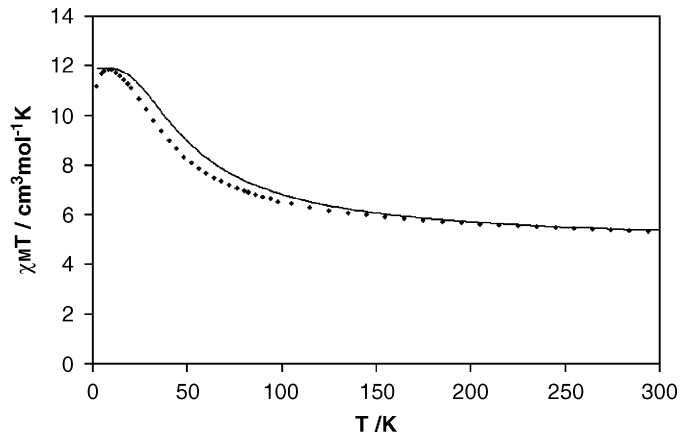


Fig. 2. Temperature dependence of the magnetic susceptibility of the Ni₄ complex. Black circles: experimental data; continuous line: calculated values.

and S_1 and S_2 are the spin values of the two interacting centres.

The calculated values for J_1 and J_2 are +13.27 and +12.86 cm^{-1} , respectively.

The calculated $\chi T(T)$ curve is presented in Fig. 2, together with the experimental data. The magnetic susceptibility data calculated using the DFT J values are in a good agreement with the experimental values at high temperatures. The difference between experimental and calculated values at low temperatures may be attributed to the fact that the anisotropy parameter was not included in the calculation. The value reported by Moragues-Cánovas et al. [6] for the separation between the $S = 4$ ground state and the first $S = 3$ excited state is 40 cm^{-1} . In our case, the energy difference is 52 cm^{-1} . The energies of the three $S = 3$ states are in the range between -26.4 and -25.6 cm^{-1} . Therefore an INS spectra should show only one peak corresponding to the transition between the ground state and the $S = 3$ states.

The electronic configuration of the paramagnetic Ni^{II} centres is $t_{2g}^6 e_g^2$ and produces an octahedral shape of the spin-density surface at the metal centres, as predicted by Ruiz et al. [19]. A high degree of delocalization of the unpaired electrons towards the μ₃-bridging oxygen atoms and, to a lesser extent towards the rest of the first coordination sphere is observed, as seen in Fig. 3.

4. Concluding remarks

The spin density is in agreement with an expected behaviour for a $t_{2g}^6 e_g^2$ electronic configuration showing a large delocalization toward the atoms of the first coordination sphere.

Moragues-Cánovas et al. reported two ferromagnetic J values which differ from each other by 7 cm^{-1} . In our study, we also found two ferromagnetic J values which differ from each other by only 0.41 cm^{-1} . The centres with J_1 show two different angles (Ni–O–Ni) with values of 97.04 and 97.95°, while the centres with J_2 interaction have

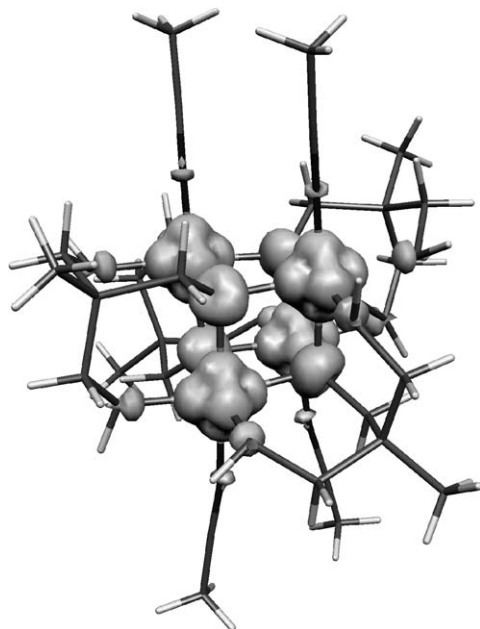


Fig. 3. Representation of the spin-density map calculated with the B3LYP functional for the $S = 4$ ground state of the complex.

both angles with the same value (97.26°). The difference between 97.26° and the average value of the other two angles, is about 0.23° . This small difference should produce similar values for J_1 and J_2 in agreement with our calculations.

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