

Theoretical studies on di- and tetra-nuclear Ni pivalate complexes†

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A combination of DFT calculations and magnetic studies allow structural features of di- and tetra-nuclear nickel pivalate cage complexes to be deduced.

Density Functional Theory (DFT) is finding increased use in molecular magnetism, *e.g.* reliable calculations of the exchange interaction, J , in transition metal clusters have been presented by Alvarez and co-workers^{1,2} and calculations of the zero-field splitting parameter, D , have been reported by Pederson and co-workers.³ We have been examining the method critically by applying it to a wide range of poly-nuclear cage complexes, preferably those where the spin Hamiltonian parameters are well established.⁴ Here we report studies on ferromagnetically-coupled, di-nuclear and tetra-nuclear Ni complexes to calculate their J values. The results are intriguing because the initial DFT calculations, based on X-ray crystal structures, seemed inaccurate, but instead have allowed us to gain a greater insight into the structures of these compounds.

We recently derived the spin Hamiltonian parameters D and J for a di-nuclear nickel complex $\text{Ni}_2(\mu\text{-O})(\text{O}_2\text{CCMe}_3)_2(\text{HO}_2\text{CCMe}_3)_6$ (**1**) using both inelastic neutron scattering (INS) and magnetic susceptibility measurements.⁵ This gives $J = +5.2 \text{ cm}^{-1}$ and $D_{S=2} = -0.725 \text{ cm}^{-1}$. The structure of **1** (Fig. 1) shows two bridging carboxylates and a bridging oxygen atom involved in H-bonding to two pivalic acid groups. The O...O distances are 2.5111 and 2.555 Å. The H-bonds make it questionable whether the structure is correctly described as $\text{Ni}_2(\mu\text{-O})(\text{O}_2\text{CCMe}_3)_2(\text{HO}_2\text{CCMe}_3)_6$ (**1A**) or $\text{Ni}_2(\mu\text{-H}_2\text{O})(\text{O}_2\text{CCMe}_3)_4(\text{HO}_2\text{CCMe}_3)_4$ (**1B**)—an issue which was unresolved by the initial X-ray diffraction experiment.⁵ We have therefore examined the issue further by using DFT calculations.

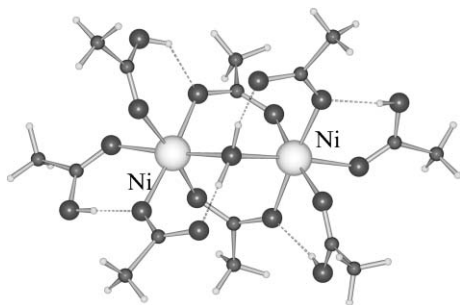


Fig. 1 The structure of model **1B**.

† Electronic supplementary information (ESI) available: Chosen spin configuration for the calculation and the coordinates of the optimised structure of **2B**. See <http://www.rsc.org/suppdata/cc/b5/b502115d/>
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All the calculations were undertaken using Gaussian,⁶ however the initial guesses for calculations were generated using Jaguar 5.0.⁷ Only single point calculations were performed using crystal structure coordinates, unless otherwise mentioned. A combination of a hybrid B3LYP function, together with the Ahlrichs triple-zeta basis set for the metal atoms and a double-zeta basis set for the others have been used.

Calculations were performed initially on a model complex of **1A**, $\text{Ni}_2(\mu\text{-O})(\text{HO}_2\text{CMe})_2(\text{HO}_2\text{CMe})_6$, replacing the pivalic acid molecules by acetic acid. For the **1A** model, a total spin multiplicity of 5 and 1 were used to calculate the energies of the high spin and broken symmetry states respectively. For the **1A** model, the DFT results gave J as $+48.7 \text{ cm}^{-1}$. Although the sign of J is reproduced, the magnitude is overestimated compared to the INS results. Calculations performed with additional functions of the TZV basis set⁸ gave J as $+50.4 \text{ cm}^{-1}$. Variation of the R group on the bridging carboxylate also failed to vary J significantly.

If we moved the H atoms of the O...H-O hydrogen bond we got a different result. A calculation on a model of **1B**, $\text{Ni}_2(\mu\text{-OH}_2)(\text{O}_2\text{CH}_3)_4(\text{HO}_2\text{CCH}_3)_4$, gave $J = +3.6 \text{ cm}^{-1}$, with the $\mu\text{-O-H}$ distances fixed at 1.0 Å. The excellent agreement with the experimental value suggests that in **1**, the bridging oxygen atom belongs to a $\mu\text{-water}$ and not a $\mu\text{-oxo}$. By coincidence, the structure of **1** had been recollected‡ and the H atom position found convincingly from a difference density map. The H atoms are attached to the bridging oxide with refined O-H distances of 0.89(2) and 0.84(2) Å. X-ray determination of O-H bonds normally underestimates the O-H distance by around 0.12 Å due to asphericity.¹⁰ The agreement with the DFT calculation is therefore excellent. The results suggest that DFT calculations, combined with INS and magnetic experiments, can be used to differentiate the bridging moiety.

The influence of the $\mu\text{-O}\cdots\text{H}$ distance on the coupling was addressed by varying the distance in the range 0.8–1.6 Å, passing from $\mu\text{-OH}_2$ to $\mu\text{-O}$. A plot of the $\mu\text{-O-H}$ distance vs. the calculated J is shown in Fig. 2. Increasing the $\mu\text{-O-H}$ distance increases the magnitude of the ferromagnetic J , the J value appearing to have an exponential relationship with the O-H distance (d): $J = 0.1^{(d/0.27)}$ (Fig. 2).

These calculations assume symmetric movement of the two hydrogens, as shown in model I of Fig. 3. However it is also possible that the two hydrogens could be antisymmetrical, as shown in model II of Fig. 3. In II, one of the hydrogen atoms is attached to the pivalic acid while the other is attached to the $\mu\text{-oxo}$ bridge. Calculations on II gave its J value as $+13.2 \text{ cm}^{-1}$, which suggests that the symmetric model is the better one.

The exponential function obtained can be understood if the spin density on the $\mu\text{-oxygen}$ or nickel atoms is considered. At longer $\mu\text{-OH}$ distances the $\mu\text{-oxygen}$ atom has a large positive spin density

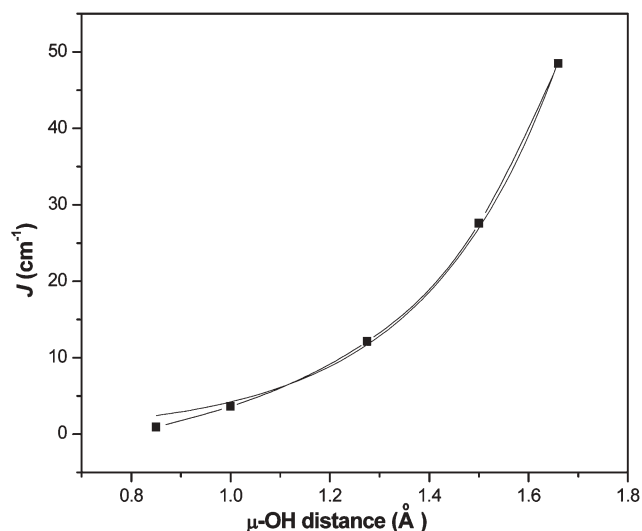


Fig. 2 Plot of μ -O-H distance vs. the calculated J values.

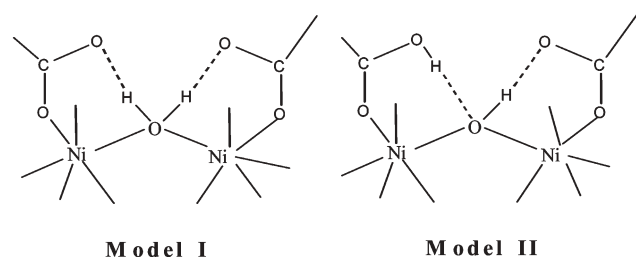


Fig. 3 Symmetric and antisymmetric movement of the hydrogen atoms.

from the spin delocalisation mechanism. This makes the ferromagnetic exchange through this group stronger. There is a corresponding decrease in the spin density on the nickel atoms if the μ -OH distance is increased.

We have also studied a tetra-nuclear Ni(II) complex, $\text{Ni}_4(\mu_3\text{-OMe})_4(\text{O}_2\text{CCMe}_3)_4(\text{MeOH})_4$ (**2**).⁵ To model INS and susceptibility data, two exchange interactions are required, $J_1 = +17.4$ and $J_2 = +9.6 \text{ cm}^{-1}$, together with $D_{S=4} = -0.282 \text{ cm}^{-1}$.⁴ The ground state is then $S = 4$. We initially performed DFT calculations to understand the parameters obtained.

Calculations were performed on a model structure $\text{Ni}_4(\mu_3\text{-OMe})_4(\text{O}_2\text{CCH}_3)_4(\text{MeOH})_4$ (**2A**). A total spin multiplicity of 9 has been used to calculate the energies of the high spin state and 1 has been used to calculate the energies of the other spin configurations. Two exchange interactions were calculated: J_1 , which is the exchange across two faces of the cubane—bridged by two μ_3 -methoxides and a carboxylate, and J_2 , which is the exchange for the other four faces—bridged by two μ_3 -methoxides in each case. Using the pair-wise interaction model⁶ gives $J_1 = +23.5$ and $J_2 = -7.4 \text{ cm}^{-1}$. The magnitude and sign of J_1 is comparable with experiment, however the interaction J_2 is antiferromagnetic—which would lead to an $S = 0$ ground state. Another model to calculate the J values, the diamagnetic element substitution method,⁶ was also tested. Here two nickel ions were replaced by diamagnetic Zn(II) ions and the calculations performed on a fictitious $\text{Ni}_2\text{Zn}_2(\mu_3\text{-OMe})_4(\text{O}_2\text{CCH}_3)_4(\text{MeOH})_4$ complex. This gave $J_1 = +17.4$ and $J_2 = -7.7 \text{ cm}^{-1}$. This double exchange

model is only an approximation as all six cubane faces are crystallographically different. However, a series of calculations considering all the J values as different gave $J_{1a} = +17.4$, $J_{1b} = +28.7$, $J_{2a} = -7.3$, $J_{2b} = -9.4$, $J_{2c} = -6.2$ and $J_{2d} = -6.5 \text{ cm}^{-1}$ (NB the average of J_{1a} and J_{1b} gives J_1 , and the average of J_{2a-c} gives J_2). In all cases, calculations based on the crystal structure gave J_2 as antiferromagnetic. This led us to question the validity of DFT for these cages.

The most significant exchange paths in **2** are probably through the methoxide bridges. Previous examples of tetra-nuclear Ni_4 heterocubanes possessing Ni–O–Ni angles above 99.0° show antiferromagnetic exchange, while more acute angles show ferromagnetic interactions.¹¹ For J_1 , the Ni–O–Ni angles involving OMe are 89.7 plus 90.2 and 87.5 plus 87.9° (average esd = 0.1°). The ferromagnetic value calculated agrees with precedence. For J_2 , the relevant angles vary between 99.4 – 100.4° (average esd = 0.1°). Previously published magneto-structural correlations¹¹ would suggest J_2 should be anti-ferromagnetic, as predicted by DFT, but in clear disagreement with measurement.

Although the J values of **2** are well-evaluated, a possible explanation for the difference between experiment, on one hand, and precedence and theory, on the other, is that the parameters may not correspond to the crystal structure. *i.e.* The powder used in measurements might have a subtle structural difference to the single crystals. In particular, the presence of two MeOH solvates bound to each nickel centre could lead to instability. Therefore, we performed a calculation whereby two terminal MeOH ligands were removed from the cubane, $\text{Ni}_4(\mu_3\text{-OMe})_4(\text{O}_2\text{CCH}_3)_4(\text{MeOH})_2$ (model **2B**), followed by structural optimisation to adjust the bonds around the new cubane. The optimised⁶ structure is shown in Fig. 4. Additionally, frequency calculations were performed on this model and the stationary point of the optimised structure was ensured. Calculations now gave $J_1 = +23.5$ and $J_2 = +1.8 \text{ cm}^{-1}$, these values fitting the experimental χT curve. The Ni–O–Ni angles corresponding to J_2 now fall into the range 93.8 – 102.3° . Other variations, for example loss of one, three or four terminal MeOH molecules, are now also possible. This suggests, but does not prove, that the previous experimental studies may have involved partially desolvated **2**. As the loss of lattice solvent or weakly bound solvate molecules can

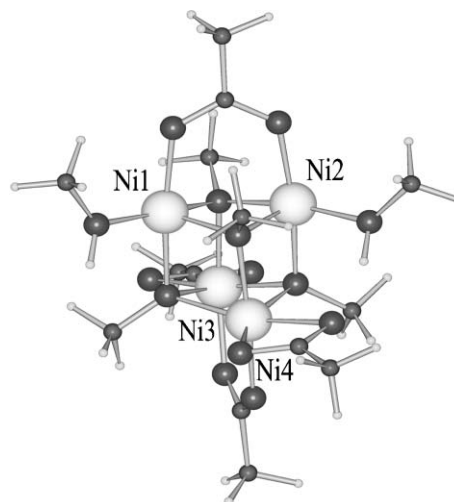


Fig. 4 The optimised structure of model **2B**.

alter magnetic behaviour, the DFT calculations performed here not only suggest such a possibility, but also allow us to make a structural prediction as to the possible alternative structure formed.

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Notes and references

‡ Crystal data for C₄₀H₇₈Ni₂O₁₇ 1: orthorhombic, Pbc_a, $a = 12.088(5)$, $b = 19.348(5)$, $c = 48.185(5)$ Å, $V = 11269(6)$ Å³, $M = 948.4$, $Z = 8$, $T = 150(2)$ K, $R1 = 0.0588$. Data collection, structure solution and refinement were undertaken using SHELXL.⁹ CCDC 268277. See <http://www.rsc.org/suppdata/cc/b5/b502115d/> for files in CIF or other electronic format.

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