An Ni_4 Single-Molecule Magnet: Synthesis, Structure and Low-Temperature Magnetic Behavior

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Keywords: Nickel / Ferromagnetism / Single-molecule studies / Cubane complexes / Tripodal ligands

The reaction of $Ni(NO_3)_2·6H_2O$ with H_3thme (trihydroxymethylethane) in the presence of NaOMe leads to a tetranuclear Ni_4 complex with a cubane-like structure. Intramolecular ferromagnetic interactions [$J = 10\ cm^{-1}$ based on $H = -J(S_1·S_2 + S_1·S_3 + S_1·S_4 + S_2·S_3 + S_2·S_4 + S_3·S_4)$] lead to an $S = 4$ ground state stabilized by 40 cm^{-1} from the first $S = 3$ excited state. Magnetization vs. field studies at different temperatures above 2 K suggest the presence of an axial magnetic anisotropy. Single-crystal magnetization measurements show a single-molecule-magnetic behavior below $T = 0.5$ K with fast relaxation of the magnetization due to resonant quantum tunneling.

Introduction

Cubane-like Ni_4 tetranuclear complexes have been extensively studied since the first report by Andrew and Blake in 1969 of a ferromagnetic interaction that lead to an $S = 4$ ground state.[1] The origin of the exchange interaction in such compounds is well-understood and is correlated to the Ni−O−Ni angle within the cubane;[1,2] ferromagnetic interaction is found when the Ni−O−Ni angle is lower than 98°.[1,3] The discovery of Single-Molecule Magnetism (SMM) in Ni(II) high spin molecular clusters[4] and particularly in cubane-like Ni_4 tetranuclear complexes[5] revived the interest in such compounds in order to study the correlation between the magnetic anisotropy of the high spin ground state and the relaxation of the magnetization at low temperature.

Here, we report on the preparation, crystal structure, and magnetic behavior of a new cubane-like Ni_4 tetranuclear complex with the general formula $[Ni_4(C_5H_{11}O_3)_4(CH_3CN)_4](NO_3)_4·1.33\ NaNO_3$, obtained using 1,1,1-trihydroxymethylethane (H_3thme) as the bridging organic ligand.

Results and Discussion

The reaction between $Ni(NO_3)_2·6H_2O$, H_3thme and $NaOCH_3$ in methanol affords, after evaporation of the solvent and extraction of the solid with acetonitrile, blue crystals suitable for structure determination (see Experimental Section). The organic ligand H_3thme has the ability to act as a terminal and/or bridging ligand depending on its degree of protonation. In the present case the single-crystal studies show that the ligand is a monoanion and the complex has a cubane-like structure. Each Ni atom of the cubane is surrounded by two protonated oxygen atoms of H_2thme^- that act as terminal atoms and by the alkoxo-like oxygen atom that bridges three Ni atoms of the cubane core. The coordination sphere of Ni is completed with one acetonitrile molecule (Figure 1). The complex has four positive charges which are compensated by four NO_3^- ions. The crystal contains Na^+ and NO_3^- ions (see formula). The molecule has a principal C_2 axis parallel to the Ni−N bonds. The geometry around Ni is slightly distorted. The shortest Ni−O distances correspond to the oxygen atoms that belong to the cubane core (2.023 and 2.043 Å), and the remaining four Ni−X distances are slightly longer (around 2.056 Å). The main distortion is due to the O−Ni−O angle within the cubane which is equal to 82.01°, while the other X−Ni−X angles are around 92°. There are three different Ni−O−Ni angles; these are equal to 97.25° for the two opposite faces and to 97.04° and 97.95° for the remaining four faces.

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DOI: 10.1002/ejic.200400129

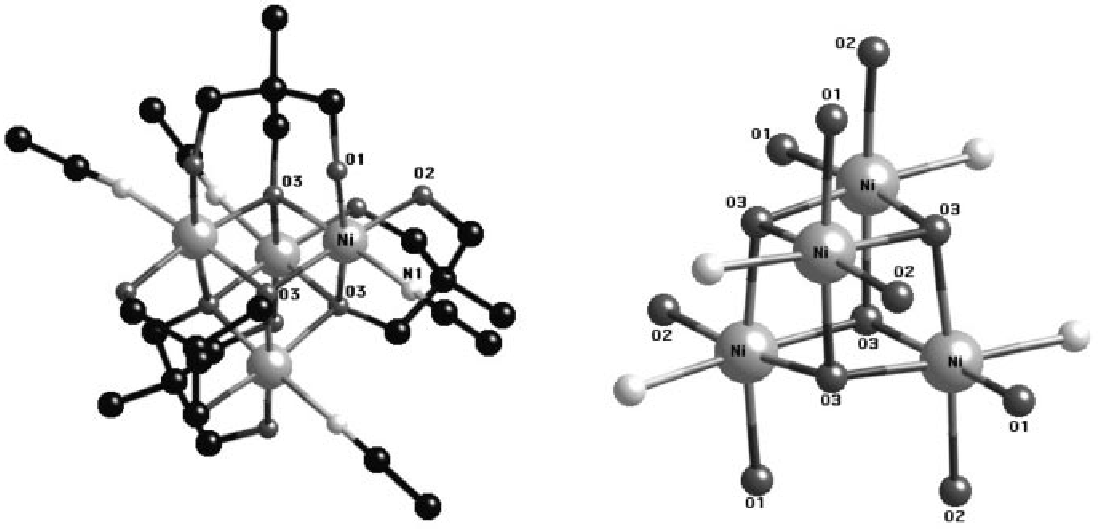

Figure 1. View of the molecular structure of Ni_4

The magnetic data which are presented in the form of $\chi_M T = f(T)$ show that the exchange interaction is ferromagnetic; the $\chi_M T$ product increases on cooling (Figure 2). The maximum $\chi_M T$ value at low temperature (11.85 $cm^3 mol^{-1} K$ at $T = 9$ K) is in agreement with that expected for a $S = 4$ ground state with a g-value larger than 2. The decrease in $\chi_M T$ below 9 K is assumed to be due to zero-field splitting within the ground state, even though the presence of weak intermolecular interactions cannot be excluded. The data were fitted to the theoretical expression of the susceptibility derived from the above-mentioned spin Hamiltonian including the Zeeman term ($g\beta HS$ where S is the spin operator corresponding to the total spin and β the Bohr Magneton) and the zero-field splitting ($D[S_z^2 - S(S + 1)/3]$ where D is the axial zero-field splitting parameter within the $S = 4$ ground state) within the $S = 4$ ground state. Therefore, we first assumed only one exchange coupling parameter between the four Ni atoms. The fit gives the following parameters: $J = 10$ cm^{-1}, $g = 2.18$, $|D| = 0.5$ cm^{-1}, and an agreement factor $R = 1.5 \times 10^{-4}$. The magneto-structural correlations for Ni_4 cubane-like complexes lead to the conclusion that a change from ferromagnetic to antiferromagnetic exchange coupling corresponds to a Ni−O−Ni angle of about 98°.[3] For the present complex there are two different sets of Ni−O−Ni angles so that two exchange coupling parameters may be used corresponding to the spin Hamiltonian (Equation 1).

$$H = -J_1(S_1 \cdot S_2 + S_3 \cdot S_4) - J_2(S_1 \cdot S_3 + S_1 \cdot S_4 + S_2 \cdot S_3 + S_2 \cdot S_4) \quad (1)$$

The fit of the magnetic data assuming two exchange parameters leads to the following results: $J_1 = 15$ cm^{-1}, $J_2 = 8$ cm^{-1}, $g = 2.18$, $|D| = 0.5$ cm^{-1}, and an agreement factor $R = 10^{-4}$. The larger ferromagnetic exchange coupling parameter (J_1) corresponds to the smaller Ni−O−Ni angles, as expected from magneto-structural correlations based on the idea that the overlap integral is weaker for angles closer to 90°. It must be stressed here that although two exchange parameters are used, the quality of the fit is not particularly improved. On the other hand, trying to fit the $\chi_M T = f(T)$ data by introducing intermolecular intercations does not lead to satisfactory results. The decrease in $\chi_M T$ at low temperature can thus be (at this level) ascribed mainly to zero-field splitting within the ground state even though the sign of D cannot usually be determined from susceptibility data on powder.

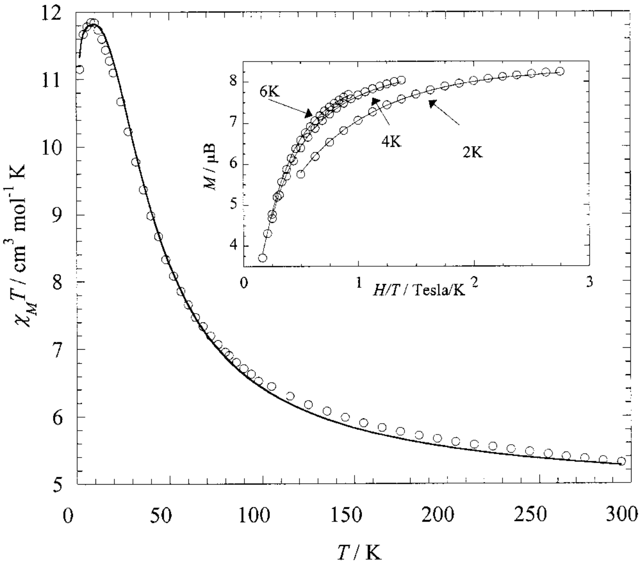

Figure 2 $\chi_M T = f(T)$ for Ni_4, the line corresponds to the best fit with $J = 10$ cm^{-1}, $g = 2.18$ and $|D| = 0.5$ cm^{-1}; inset: $M = f(H/T)$ for Ni_4 for $T = 2$, 4 and 6 K, the lines correspond to the best fit with $D = -0.43$ cm^{-1}, $E/D = 0.04$ and $g = 2.22$

In order to have a better estimation of the zero-field splitting parameters, magnetization vs. field studies at $T = 2$, 4 and 6 K were carried out. The $M = f(H/T)$ plots for H between 1 and 5.5 Tesla (Figure 2 inset) are not superimposable and therefore indicate the presence of magnetic anisotropy within the ground state. Since the $S = 3$ first excited state is separated by about 40 cm^{-1} from the ground state, we assume that only the ground state is responsible for the magnetization response. The magnetization data were fitted by diagonalizing the energy matrix for different orientations of the magnetic field. Two reasonable sets of parameters may be obtained depending on the starting values: $D = -0.43\ cm^{-1}$, $E/D = 0.04$, $g = 2.22$, $R = 2 \times 10^{-5}$ and $D = -0.48\ cm^{-1}$, $E/D = 0.23$, $g = 2.25$, $R = 6.6 \times 10^{-5}$. It is not unusual to find more than one set of parameters with very different E/D values since the E parameter has little influence on the shape of the $M = f(H)$ plots. However, the D values as found are generally very close and can be considered as very good estimates of the magnetic anisotropy of the ground state. The negative sign of D indicates that there is an easy magnetization axis. In such a case one may expect a blocking of the magnetization as a result of a long relaxation time at low temperature.[6] On the other hand, it is well-understood that the magnitude of the E parameter which defines the deviation from purely axial anisotropy is crucial for relaxation by a quantum tunneling process. For large E/D values it is expected that fast relaxation occurs at $H = 0$ and at low temperatures because of the relatively large mixing between the low-lying $M_S = +4$ and -4 sublevels. This may completely preclude the observation of a hysteresis loop in the magnetization plots. However, for weak rhombicity (E/D close to zero) relaxation by quantum tunneling may occur, but not fast enough such that hysteresis may still be present.[7]

In order to get insight into the behavior at very low temperatures, magnetization studies were carried out on a single-crystal using an array of micro-SQUIDs.[8] The measurements were performed with the magnetic field parallel to the easy axis of the crystal. The applied magnetic field was swept at different rates between -1 and 1 Tesla and then back to -1 Tesla at different temperatures between 0.4 and 0.04 K. The data obtained at a sweep rate of 0.14 Tesla/s show a hysteresis loop which includes two steps: a broad one at about 0.3 Tesla and the other very close to zero (Figure 3). The presence of a hysteresis loop indicates that below $T = 0.4$ K, the magnetization is blocked. However, the presence of two steps is the result of rapid relaxation of the magnetization at a given magnetic field where level crossing is avoided. As the temperature decreases, the number of molecules that undergo relaxation by thermal activation diminishes and those that undergo relaxation by tunneling increases. The result is a narrowing of the hysteresis loop with steeper steps. This observation is seen in the present Ni_4 complex. In order to confirm the quantum tunneling of the magnetization, measurements were performed at $T = 0.04$ K for different sweep rates of the magnetic field. The magnetic field was set at $H = -1$ Tesla and then swept towards $H = 1$ Tesla (Figure 4). At $H = -1$ Tesla, all the molecules are in the $M_S = +4$ state. When the magnetic field reaches zero, there is resonance between the $+4$ and the -4 M_S levels and part of the molecules tunnel to $M_S = -4$, while the remaining stay in the former state. This explains the observation of a step at $H = 0$. The height of the step indicates that the tunneling process is relatively fast and thus there is sufficient mixing of the low-lying $M_S = +4$ and -4 levels. On increasing the field above zero, one expects another step corresponding to the molecules tunneling from the $M_S = +4$ to the $M_S = -3$ sublevel. This should occur when H is very close to $D/g\beta$ (about $H = 0.41$ Tesla).[9] A step is actually observed, but at a field closer to 0.32 Tesla. Furthermore, the step is not very steep and this may be due to the presence of different tunneling processes that are not resolved. One possible explanation for such a shift is the presence of very weak intermolecular interactions (exchange or dipolar).[10,11] The tunnel probability de-

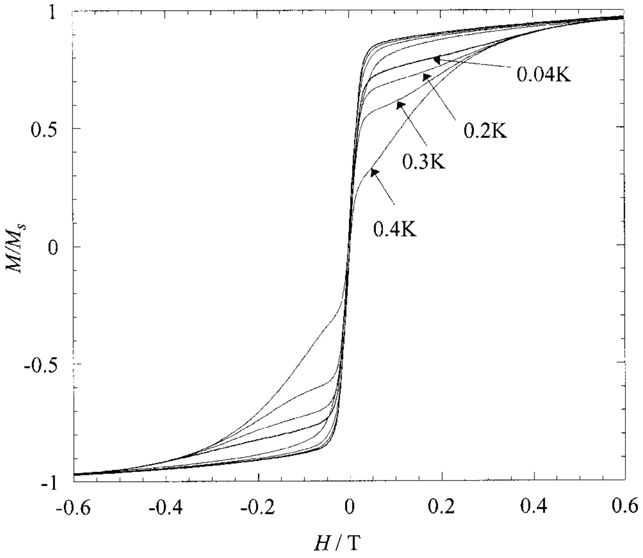

Figure 3. $M/M_S = f(H)$ for a single crystal of Ni_4 with H parallel to the easy axis at different temperatures

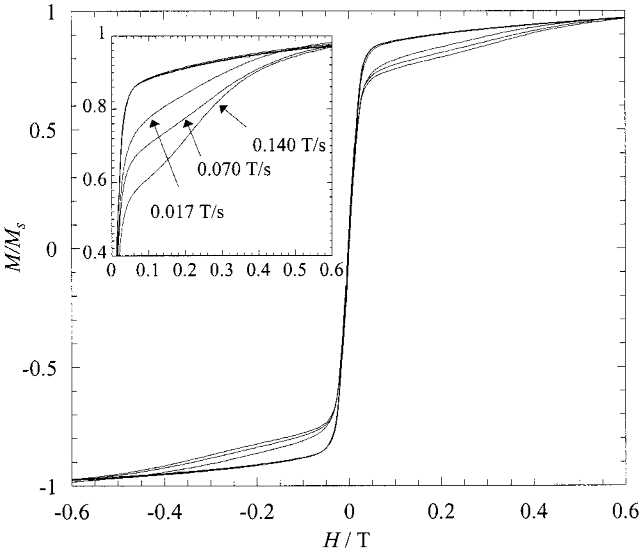

Figure 4. $M/M_S = f(H)$ for a single crystal of Ni_4 with H parallel to the easy axis at different sweep rates of H from -1 to 1 Tesla and back to -1 Tesla; inset: $M/M_S = f(H)$ for a single crystal of Ni_4 with H parallel to the easy axis at different sweep rates of H from 0 to 1 Tesla and back to 0 Tesla

creases when the sweep rate is increased,[12] therefore, when the same experiment is carried out at higher sweep rates, the number of molecules tunneling at zero field is less important and the hysteresis loop is larger as shown in Figure 4.

The width of the hysteresis loop depends on the magnetic "history" i.e. the starting magnetic state before varying the magnetic field. Thus, when the field is swept from zero rather than from -1 Tesla ($T = 0.04$ K), the hysteresis is larger (Figure 4 inset). This can be understood by the fact that there are an almost equal number of molecules in the $M_S = -4$ and $M_S = +4$ states when starting at zero field. When the field is increased from zero, the number of molecules that stay in the $M_S = +4$ state is larger than when the field is swept from $H = -1$ Tesla, resulting in a larger hysteresis. This is true especially for systems with relatively fast relaxation by tunneling processes, as is the case for the present complex.

From the above studies, one may conclude that the Ni_4 complex presents a rich magnetic behavior at low temperature. The magnitude of the rhombicity is clearly weak and a value of E/D of about 0.04 seems more reasonable than 0.23. High-field high-frequency EPR studies are underway in order to accurately determine the spin Hamiltonian parameters D and E and confirm the magnitude of the transverse anisotropy term E responsible for the resonant tunneling at very low temperatures.

Experimental Section

Synthesis: Solid H_3thme (137 mg, 1.14 mmol) and $NaOCH_3$ (185 mg, 3.4 mmol) were added to a solution of $Ni(NO_3)_2 \cdot 6\,H_2O$ (1 g, 3.4 mmol) in methanol (25 mL). The mixture was stirred at room temperature for 24 h, affording a dark green solution which was evaporated to dryness. Extraction of the green powder with 15 mL of MeCN afforded blue crystals suitable for X-ray diffraction. $C_{28}H_{56}N_{9.33}Na_{1.33}Ni_4O_{28}$; $M = 1236.98$ g mol^{-1}; anal. calcd Na 1.90, Ni 19.43; ; found Na 1.20, Ni, 19.4.

General Remarks: Crystal data: $C_{28}H_{56}N_{9.33}Na_{1.33}Ni_4O_{28}$, $M = 1236.98$, cubic, $a = 24.190(3)$ Å, $U = 14155(3)$ Å^3, $T = 100$ K, space group $I\text{-}43d$, $Z = 12$, Mo-$K(\alpha1) = 0.71069$ Å, 16171 reflections measured, of which 2091 were unique ($R_{int} = 0.1176$). The structure was solved by direct methods (SHELXS-97) and refined with SHELXL-97.[13,14] The final conventional R-factor (based on F and 1876 data with $F > 4(F)$) was 0.0841.

CCDC-233996 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

The authors thank the ESF (Programme Molecular Magnets), the European Union (TMR network "Molecules as Nanomagnets" HPRN-CT-1999-00012) and the EPSRC(UK) for financial support.

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Received February 11, 2004