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The Case of Symmetry-Dependent Ground-State Spin Value in Ni(II) Clusters of High-Nuclearity. Crystal Structure and Magnetic Properties of a Pentanuclear and a Nonanuclear Ni(II) Clusters

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The crystal structures and the magnetic properties of a pentanuclear (**1**) and a nonanuclear (**2**) Ni(II) clusters are described. In the former, crystallizing in the cubic *I*23 space group, the Ni(II) assembly is composed of a regular tetrahedral geometry of four metal ions centered on the fifth. The nonanuclear cluster crystallizes in the hexagonal crystallographic system – *R*3 space group – the Ni(II) assembly is composed of two regular tetrahedra, like that of the pentanuclear cluster, sharing a common apex. All metal ions in either cluster are six-coordinate. Variable-temperature magnetic susceptibility data show antiferromagnetic interactions for both clusters. Moreover, magnetization data are in line with uneven intermediate-spin ground states [S=1, S=2] and [S=2, S=3] for **1** and **2**, respectively. A comparison of both the symmetry and the spin ground state of **1** to those of lower-symmetry pentanuclear Ni(II) clusters, reveals that the ground-state spin value increases with the cluster symmetry.

Keywords: pentanuclear; nonanuclear; Ni(II) clusters; benzotriazolate ligands

INTRODUCTION

In a preliminary report[1] we had presented the X-ray crystal structure and brief magnetic results of $[Ni_5(OH)(bta)_5(acac)_4(H_2O)_4]$, (**3**; btaH = benzotriazole, acacH = acetylacetone), a cluster consisting of a tetrahedral arrangement of four six-coordinate Ni(II) ions centred on the fifth. In the subsequent full paper[2] we reported in more detail on the magnetic properties of **3**, together with those of

the higher symmetry analogue $[Ni_5(OH)(5,6diMebta)_5(acac)_4(H_2O)_4]$, (**4**; 5,6diMebtaH = 5,6-dimethylbenzotriazole). Both clusters indicated antiferromagnetic interactions which were interpreted using a 5-*J* magnetic model, based on the hierarchy of algebras approach. It was the first time that both a solution for a Hamiltonian involving five different exchange parameters and its application on real low-symmetry magnetic systems have been attempted. Magnetization data for both clusters showed an intermediate ground state (S=0, S=1), revealing that the ground-state spin value increases as the symmetry of the cluster increases. In an attempt to further verify this preliminary conclusion, we report herein on the preparation, crystal structure and magnetic properties of the totally symmetric pentanuclear Ni(II) cluster, $[Ni_5(5Mebta)_6(dbm)_4(Me_2CO)_4]$ (**1**; 5MebtaH = 5-methylbenzotriazole; dmbH = dibenzoylmethane) along with those of a novel nonanuclear one, $[Ni_9(5,6diMebta)_{12}(bzac)_6(MeOH)_6]$, (**2**; bzacH = benzoylacetone). Both **1** and **2** do reveal higher intermediate-spin ground states than **3** and **4**. The reason for this magnetic behaviour is discussed.

EXPERIMENTAL SECTION

Physical Measurements

Magnetic and EPR measurements were carried out as previously described[1,2].

Preparation of the complexes

$[Ni_5(5Mebta)_6(dbm)_4(Me_2CO)_4].4Me_2CO$ ($1.4Me_2CO$). To a warm slurry of $[Ni(dbm)_2(EtOH)_2]$ (0.32 g, 0.54 mmol) in Me_2CO (20 ml) was added a solution of 5MebtaH (0.09g, 0.65 mmol) in the same solvent (5 ml). The Ni(II) starting material rapidly dissolved and the resulting green solution was layered with an equal volume of n-hexane. Slow mixing yielded well-formed, X-ray quality green prisms of $1.4Me_2CO$. Typical yields are in the 70-80% range. A sample for crystallography was kept in contact with the mother liquor to prevent lattice solvent loss. Collection of the crystals by filtration, washing with Et_2O, and dried in vacuo over silica gel leads to the unsolvated form **1**. Anal. calcd (found) for $C_{114}H_{104}N_{18}O_{12}Ni_5$: C, 61.9(61.8); H, 4.7(4.6); N, 11.4 (11.5); Ni, 13.3(13.7) %.

$[Ni_9(5,6diMebta)_{12}(bzac)_6(MeOH)_6].3H_2O$ ($2.3H_2O$). To a green so-

lution of $[Ni(bzac)_2(EtOH)_2]$ (0.33 g, 0.70 mmol) in MeOH (20 ml) was added a solution of 5,6diMebtaH (0.13g, 0.87 mmol) in the same solvent (6 ml). The resulting olive green solution was refluxed for 30 min and left undisturbed at room temperature for 48 h. Green crystals of the product were precipitated, collected by filtration, washed with Et_2O, and dried in vacuo over P_4O_{10}. Typical yields are in the 75-85% range. A sample for crystallography was kept in contact with the mother liquor to prevent lattice water loss. The crystals established the formulation **2**.$3H_2O$; the dried sample analyzed for **2**. Anal. calcd(found) for $C_{162}H_{174}N_{36}O_{18}Ni_9$: C, 56.5(56.3); H, 5.1(5.1); N, 14.7(14.5); Ni, 15.3 (15.7) %.

X-ray Crystallography

Green crystals of **1**.$4Me_2CO$ and **2**.$3H_2O$ with approximate dimensions 0.20 ×0.20×0.40 mm and 0.20×0.50×0.50 mm, respectively, were mounted in capillary. Diffraction measurements were made on a Crystal Logic Dual Goniometer diffractometer using graphite monochromated Mo radiation. We strongly suspected that the crystals of both complexes were twinned; however, we were able to find unit cells and proceeded with data collection. Unit cell dimensions were determined and refined by using the angular settings of 25 automatically centered reflections in the ranges $11<2\vartheta<23°$ (**1**.$4Me_2CO$) and $11<2\vartheta<24°$ (**2**.$3H_2O$). Intensity data were recorded using a ϑ-2ϑ scan. For **1**.$4Me_2CO$: f.w.=2444.09, cubic, $I23$, a=19.034(5) Å, V=6896 Å^3, Z=2, reflections collected(unique/used) 6165/1929 (R_{int}=0.0553)/1928, 83 parameters refined, 2ϑ(max) = 53°, scan speed 2.5 °/min, scan range 2.4 plus $\alpha_1\alpha_2$ separation; for **2**.$3H_2O$: f.w.=3495.86, hexagonal, $R\bar{3}$, a=25.220 Å, c=39.002(3) Å, V=21484(3) Å^3, Z=3, reflections collected(unique/used) 11609/7563 (R_{int}=0.0372)/7537, 348 parameters refined, 2ϑ(max) = 48.5°, scan speed 2.2 °/min, scan range 2.5° plus $\alpha_1\alpha_2$ separation. Three standard reflections monitored every 97 reflections showed less than 3% fluctuation and no decay. Lorentz polarization and Ψ scan absorption (only for **2**.$3H_2O$) corrections were applied using Crystal Logic software.

The structures were solved by direct methods using SHELXS-86[13] and refined by full-matrix least-squares techniques on F^2 with SHELXL-93[14]. Refinements proceeded to $R1/wR2$=0.1041/0.2768 and 0.0779/0.2270 for **1**.$4Me_2CO$ and **2**.$3H_2O$, respectively (R values refer to the observed reflections with $I>2\sigma(I)$). However, while the metal ions and the benzotriazolate ligands are well

behaved with good bond lengths and angles, and acceptable esds' the other ligands are not. In **1**.4Me_2CO only the Ni atoms and those of Mebta$^-$ (with the exception of the methyl group which is disordered) were refined anisotropically; the carbon skeleton of the Me_2 CO and dbm$^-$ ligands on Ni(2) is disordered over three sites, due to the 3-fold axis going through Ni(2), and their atoms were refined isotropically. No H-atom were included in the refinement. In the case of **2**.3H_2O, there is a positional disorder between the diketonate ligand and the methanol coordinated to Ni(3). The diketonate anion is anchored to Ni(3) through O(1), while O(2) shifts to two coordination sites which it shares the methanolic oxygen [O(3)]. The phenyl ring of the disordered bzac$^-$ is fixed to a regular hexagon. All non-H atoms, except those of the disordered phenyl ring of bzac$^-$, were refined anisotropically. Of the existing H-atoms, H(7) and H(14) were located by difference maps and those of the methyl groups C(20) and C(21) were introduced at calculated positions as riding on bonded atoms; the rest were not included in the refinement.

RESULTS AND DISCUSSION

Molecular Structures

ORTEP representations of **1** and **2** are shown in Figures 1 and 2, respectively; a full list of bond distances and angles are given as Supplementay Material (Tables S3 and S4). The pentanuclear Ni(II) assembly of **1** is composed of a tetrahedral arrangement of four six-coordinate Ni(II) ions [Ni(2)], centred on the fifth [Ni(1)]. Each of the six μ_3–5Mebta$^-$ ligands spans an edge of the Ni_4 tetrahedron and is ligated to the central metal through its central nitrogen atom [N(2)]. A terminal Me_2CO molecule and a chelating dbm$^-$ ligand complete octahedral coordination at each peripheral metal. The molecule lies on three crystallographically-imposed, mutually perpendicular 2-fold axes passing through N(2) and Ni(1) and, as a result, only half of the 5Mebta$^-$ ligand is crystallographically independent. The peripheral metal [Ni(2)] lies on a 3-fold axis which is parallel to one of the body diagonals of the cube. Due to the high symmetry of **1**, the coordination polyhedron around Ni(1) is a perfect octahedron.

The central metal site [Ni(1)] of **2** lies on an inversion axis (3), i.e., Ni(1) is on a centre of symmetry and there is also a crystallographic 3-fold axis passing through Ni(2) and Ni(1). The nonanuclear molecule is composed of two almost

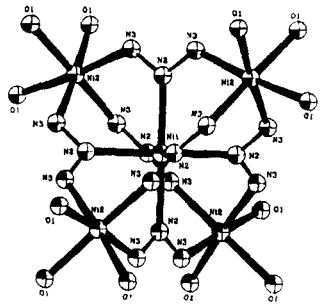

FIGURE 1 ORTEP view of **1** showing the atom labeling scheme. To avoid congestion, all carbon atoms are omitted. Identical numbers are used for the symmetry-related Ni and N atoms, and for the O atoms of the disordered Me_2CO and dbm$^-$ ligands. Distances (Å): Ni(1)...Ni(2) 3.706(1), Ni(2)...Ni(2),6.049(1), Ni(1)...N(2) 2.134(9), Ni(2)...N(3) 2.069(8), Ni(2)...O(1) 2.061(13)

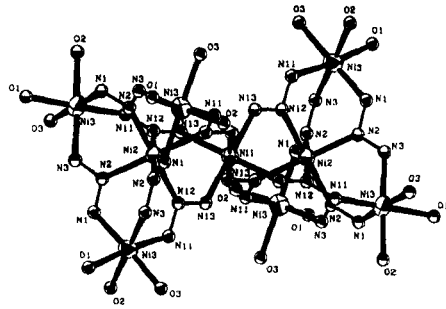

FIGURE 2 ORTEP view of **2** showing the atom labeling scheme. To avoid congestion, all carbon atoms are omitted. Identical numbers are used for the symmetry-related atoms. Distances (Å): Ni(1)...Ni(2) 3.709(1), Ni(2)...Ni(3) 3.682(1), Ni(3)...Ni(3) 6.018(1), Ni(1)...Ni(3) 6.029(1), Ni...N 2.039(5) - 2.134(4), Ni(3) - O 2.110(6) and 2.112(5).

perfect tetrahedral arrangements of Ni(II) ions [Ni(1), Ni(3), Ni(3), Ni(3)] centr-

ed on a fifth [Ni(2)]; the two tetrahedra have a common apex at Ni(1). A terminal MeOH molecule and a chelating bzac$^-$ ligand complete a distorted coordination at the peripheral metals [Ni(3)]. The 5,6diMebta$^-$ ions behave as μ_3 ligands. The $Ni(1)N_6$ and $Ni(2)N_6$ coordination spheres are almost perfectly octahedral.

Magnetic Susceptibility Studies

Variable-temperature (4.2-295 K) magnetic susceptibility data were collected on powder samples of both **1** and **2** at 1000 G and 6000 G. The variation with temperature of both χ_M and the $\chi_M T$ product for **1** is illustrated in Figure 3. The room temperature $\chi_M T$ value (1.05 cm^3 mol^{-1} K) is close to that expected for an S=1 Ni(II) ion. Moreover, $\chi_M T$ decreases gradually with the decreasing temperature and is ca. 0.405 cm^3 mol^{-1} K at 4.2 K. The room temperature $\chi_M T$ value (1.20 cm^3 mol^{-1} K) of **2** (shown in Figure 4) is again close to that expected for an S=1 Ni(II) ion. $\chi_M T$ decreases again gradually with the decreasing temperature, and becomes ca. 0.39 cm^3 mol^{-1} K at 4.2 K. Antiferromagnetic interactions are characterized by a regular decrease of $\chi_M T$. The interaction is most likely intramolecular, because both benzotriazolato and acetylacetonato ligands should afford good intercluster magnetic shielding.

Due to the high symmetry of **1** and **2** a 2-J theoretical model is used to interpret their magnetic susceptibility data. For the former the Kambe method is used to obtain the eigenvalues of the isotropic HDvV Hamiltonian, and an approxima-

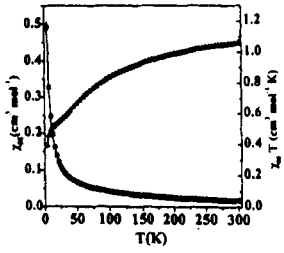

FIGURE 3 Plots of χ_M and $\chi_M T$ versus T for a polycrystalline sample of **1**. The solid line represents the fit to the theoretical model.

te one for the latter cluster (see Appendix). By assuming[2] equal the spectroscopic splitting constant, g for all the individual nickel(II) ions, a very small and negative zero-field splitting, negligible the intercluster exchange parameters and

by fixing Nα at 400×10^{-6} cm^3 mol^{-1} an excellent fit is obtained for **1** (solid line in Fig. 3) from the following set of parameters: J_1 = -3.1(1), J_2 = -10.1(1) cm^{-1}, g=2.1(1); those for **2** are J_1 = -3.1(1), J_2 = -7.10 cm^{-1} and g = 2.8(1) (solid line in Fig. 4); J_1 is the exchange parameter between the peripheral Ni(II) ions, J_2 that between the central and the peripheral Ni(II) ions in the former, and the

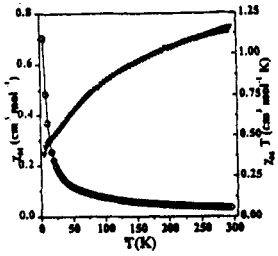

FIGURE 4 Plots of χ_M and $\chi_M T$ versus T for a polycrystalline sample of **2**. The solid line represents the fit to the theoretical model.

same numbering for the J parameters was kept for the latter concerning each one of the two tetrahedral pentamers sharing a common apex. The approximate method used for the derivation of the eigenvalues for **2** is based on the random selection of 3^5 eigenstates from the total energy spectrum of the 3^9 ones; the two consequences of this are the unusual high g value of 2.8(1) derived from the fitting procedure and the inability to have the energy spectrum of **2**. However, the energy spectrum of **1**, can be obtained by using its fitting parameter values in the magnetization equation; the thus derived ground state is a triplet with a quintet 4 cm^{-1} higher in energy.

The antiferromagnetic exchange interactions, present in the two pentanuclear Ni(II) clusters exhibiting the lower symmetry, **3** and **4**, were explained[2] on simple symmetry considerations and with the aid of quantum-chemical calculations. Within this framework, it could be also assumed that, **1** consists of several hypothetical benzotriazolate-bridged Ni(II)-Ni(II) dimers. Due to the high symmetry of **1**, the only two hypothetical dimers, which should be considered, are the Ni(1)-Ni(2) and Ni(2)-Ni(2) ones, corresponding to the - 10.1 and - 3.1 cm^{-1} J-values, respectively, derived from the fitting procedure. The three bridges for the former dimer (see Fig. 1) are the three N(2)-N(3) diatomics of three different

benzotriazolate ligand-bridges, the only triply-bridging unit between the two Ni(II) ions in the latter is that of a N(3)-N(2)-N(3) moiety of a benzotriazolate ligand. The three doubly-bridging benzotriazolato ligands along with the shorter Ni...Ni distance could account well for the higher J value derived for the former. As far as the J values derived for **2** are concerned, they could be also explained in a quite analogous way to that of **1**.

Magnetization and EPR Studies

In an attempt to verify further both the nature of the ground states of **1** and **2**, as well as the symmetry-dependence of their ground states – this latter was also seen in a recent paper of ours[2] for two analogous Ni(II) clusters, **3** and **4** of lower symmetry – the field dependence of their magnetization was also recorded at 3 K and 4 K in the 0-5 T field range, (see Figures 5 and 6). The magnetization

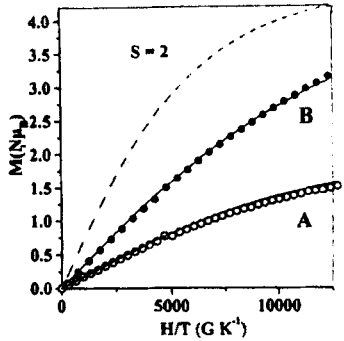

FIGURE 5 Magnetization study of **1** (B) and **4** (A) at 3 K over the 0-5 T. (See text for details).

measurements of the lowest symmetry cluster, **3** (Space Group: P-1) show[2] an intermediate-spin ground state. In particular, **3** shows a triplet ground state, whereas a singlet is only 0.3 cm^{-1} higher in energy; the singlet-triplet energy gap for the higher-symmetry (space group: C2/c) cluster **4**, is 3 cm^{-1}. Moreover, in **4** the triplet ground state is well isolated, whereas the Brillouin function for a triplet is more in line with the experimental data. However, a more significant deviation of the Brillouin function from the experimental data is obvious for **3**. These data clearly show that, on going from lower to higher symmetry the ground state of the system increases.

In the present paper we use a modified magnetization equation to fit the magnetization data. In particular, by taking into account the values of the energy differences derived from the susceptibility fitting, the equation of the magnetization (by definition) is:

$$M = \frac{\sum_i \mu_i e^{-E_i/kT}}{\sum_i e^{-E_i/kT}}$$

where, E_i are the eigenvalues and μ_i the microscopic magnetization of the i state. The magnetization data of **4** and **1**, along with their theoretical curves using the above equation are shown in Figure 5. In particular, in the case of **4** – in which the S=1 (E_1=0) and the first excited state S=0 (E_2=3 cm^{-1}) derived from the susceptibility measurements[2] are taken into account – an excellent fit is obtained. In the case of **1**, we also take into account the energy difference, derived from the susceptibility measurements, between the ground state S=1 (E_1 = 0) and the first excited state S=2 (E_2=4 cm^{-1}). The solid lines in Figure 5 are the theoretical curves derived from the above mentioned equation and the dotted line represents the Brillouin function for an S=2. It is important to note that in similar cases, in which a number of spin states are very close in energy to the ground state, the susceptibility measurements are strongly emphasized by replacing their results to the above magnetization equation. Nevertheless, the inclusion of more excited states in the same equation has a minor contribution. The results of **1** – in which both the symmetry and the ground state (S=2) have been increased – verify further our previous[2] conclusion concerning the increase of the ground

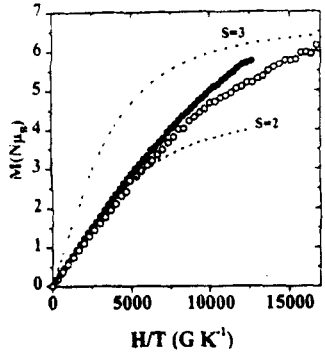

FIGURE 6 Magnetization study of **2** at 3 K (closed circles) and 4 K (open circles) over the 0 - 5 T. (See text for details).

state of the three Ni(II) pentanuclear clusters with the increase of the symmetry.

Despite the ignorance of the energy spectrum of **2**, it is obvious that (Figure 6), its ground state has been increased more and – according to the magnetization data – it is also of indermediate-spin character [S=2, S=3]. The dotted lines in Fig. 6 represent the Brillouin functions for S=2, S=3. Another important feature to emerge from Fig. 6 for **2** is that the magnetization data for T=3 K and T=4 K are not superimposed despite the temperature-independence of M=f(H/T). This reveals the non-Brillouin character of the depopulation which clearly diverges from Boltzmann statistics. In all other complexes **1**, **3**, **4** the curves are superimposed for T=3K, 4 K. An intermediate-spin ground state has also been observed in other high-nuclearity spin clusters[2].

The presence of a state with an integer spin value which is thermally populated at 4.3 K is confirmed by the EPR spectra of both **1** and **2**. As a matter of fact, they both show a low-field intense transition (ca. 1000 G) due to zero-field splitting effects[5] between the S=1 and S=2 levels for **1**, and between the S=2 and S=3 levels for **2**. Moreover, the fact that the low-field transitions are more intense than the high-field ones is in line with a negative and small D value[6] in excellent agreement with the assumption made for the D value in the fitting procedure.

Supplementary Material
Tables S1-SVIII, listing crystal and refinement data, positional and equivalent thermal parameters of the non-hydrogen atoms, bond lengths and angles, and anisotropic thermal parameters of the non-hydrogen atoms (16 pages), as well as the Magnetic Appendix (2 pages), are available from the authors (E.G. B.) upon request.

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