Benzotriazolate-mediated Assembly of the Discrete Asymmetric Pentanuclear Nickel Complex $[Ni_5(OH)(bta)_5(acac)_4(H_2O)_4]$ (Hbta = benzotriazole, Hacac = pentane-2,4-dione)

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Reaction of $[Ni(acac)_2(H_2O)_2]$ with benzotriazole (Hbta) in acetone–*n*-hexane yields the pentanuclear nickel complex $[Ni_5(OH)(bta)_5(acac)_4(H_2O)_4]$ **1**; the novel structure of this compound is described, together with the results of magnetic susceptibility studies which indicate antiferromagnetic coupling between the nickel(II) ions within the complex.

The coordination chemistry of benzotriazoles is currently an area of great activity.[1–3] One reason for this is the anticorrosion action of benzotriazole and substituted benzotriazoles towards certain metals, particularly copper and its alloys.[4] Moreover, 3d-metal benzotriazolate clusters encompass a range of interesting structural types[1,3,5] and, quite frequently, possess unusual magnetic properties and spectroscopic characteristics.[1,6–9]

More recently, we have developed an interest in nickel benzotriazoles,[10] an area that has been relatively unexplored for this otherwise well-studied metal and we report herein the preparation of the remarkable $[Ni_5(OH)(bta)_5(acac)_4(H_2O)_4]$ compound with a rare nuclearity of five. It is also the first example of a pentanuclear nickel(II) complex to be magnetically characterized.

A blue-green solution of $[Ni(acac)_2(H_2O)_2]$ in acetone–H_2O (95 : 5, *v*/*v*) was treated with 1 equiv. of benzotriazole (Hbta) under reflux for 30 min. The resulting deep blue solution was filtered and *n*-hexane was added to the filtrate. The filtrate was allowed to concentrate by slow evaporation to give blue crystals of $[Ni_5(OH)(bta)_5(acac)_4(H_2O)_4]\cdot 4Me_2CO\cdot 0.5C_6H_{14}$ ($\mathbf{1}\cdot 4Me_2CO\cdot 0.5C_6H_{14}$) in low yield (15%).†

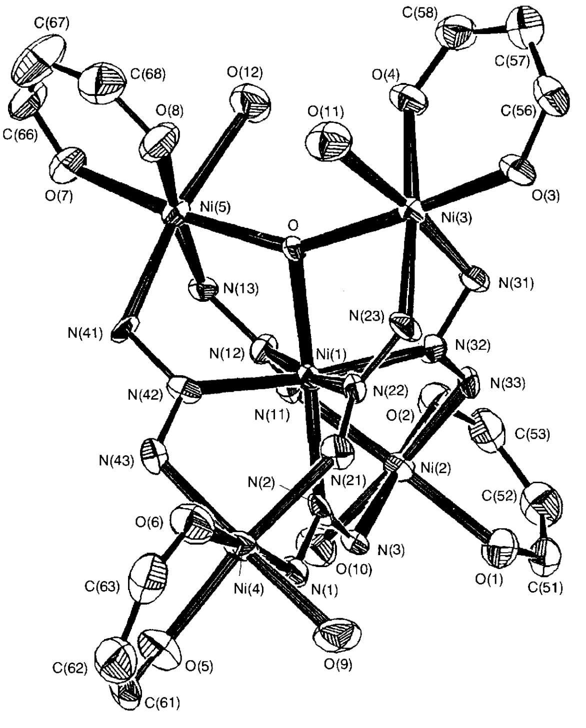

Fig. 1 ORTEP representation of complex **1**. To avoid congestion, the methyl groups of acac⁻ and all benzotriazolato carbon atoms are omitted. Selected distances (Å) and angles (°): Ni(1)–O 2.044(7), Ni(1)–N(2) 2.065(8), Ni(2)–O(1) 2.024(8), Ni(3)–O 2.063(7), Ni(3)–N(31) 2.081(9), Ni(4)–O(9) 2.175(8), Ni(5)–O 2.076(7), Ni(5)–N(41) 2.124(9), Ni(1)···Ni(2) 3.648(2), Ni(1)···Ni(5) 3.269(2), Ni(2)···Ni(4) 6.072(2), Ni(3)···Ni(5) 3.987(2); Ni(1)–O–Ni(3) 105.5(3), Ni(3)–O–Ni(5) 148.6(4), O(5)–Ni(4)–O(6) 89.6(3), Ni(2)···Ni(1)···Ni(3) 116.4(4), Ni(2)···Ni(1)···Ni(4) 112.8(4), Ni(3)···Ni(1)···Ni(5) 75.1(6).

The structure of the product was determined by X-ray crystallography.‡ The asymmetric pentanuclear nickel(II) assembly of **1** (Fig. 1)is composed of a distorted tetrahedral arrangement of four six-coordinate Ni^{II} atoms [Ni(2), Ni(3), Ni(4), Ni(5)] centred on the fifth [Ni(1)]. Each of the five μ_3-bta^- ligands spans an edge of the Ni_4 tetrahedron and is ligated to the central nickel [Ni(1)] through its central nitrogen atom. The OH^- ion bridges Ni(1), Ni(3) and Ni(5), and spans the sixth edge [Ni(3)···Ni(5)] of the tetrahedron. A chelating $acac^-$ group and a terminal water molecule complete octahedral coordination at each peripheral metal. The short Ni(3)···Ni(5) distance (3.987 Å) is a result of the presence of a *monatomic* bridge between these two Ni^{II} atoms.

The observed $\eta^3 : \mu_3$ mode of bta^- is extremely rare and was seen previously only in copper[3,10] and thallium[11] chemistry. The structure of complex **1** bears resemblance to that of $[Cu_5(bta)_6(acac)_4]$ **2**.[3] The latter contains an extra bta^- group, instead of the μ_3-OH^-, spanning the sixth edge of the Cu_4 tetrahedron. Complex **1** joins a small family of discrete pentanuclear nickel(II) clusters (see, for example, ref. 12).

Variable-temperature, solid-state, magnetic susceptibility studies have been performed on a powdered sample of **1** in the 5.0–295 K temperature range (Fig. 2) using a SQUID magnetometer. The effective magnetic moment per Ni^{II}, μ_{eff}/Ni, steadily decreased from 2.85 μ_B at 295 K to 1.15 μ_B at 5.0 K, which indicates the presence of an antiferromagnetic exchange interaction between the Ni^{II} ions.

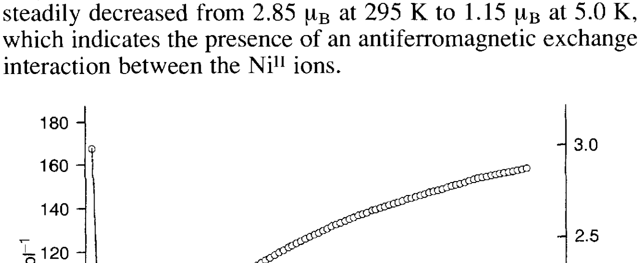

Fig. 2 Plots of the molar magnetic susceptibility, χ_M, and effective magnetic moment per nickel(II) ion, μ_{eff}/Ni, *vs*. *T* for a polycrystalline sample of complex **1**. The solid line results from a least-squares fit of the susceptibility data to the theoretical model; see text for fitting parameters.

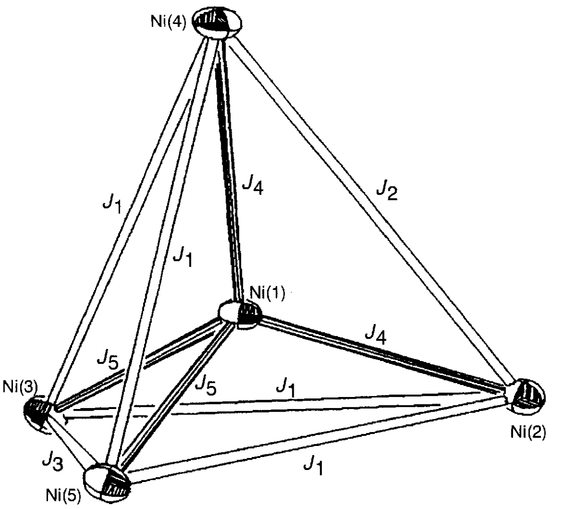

Fig. 3 Schematic drawing representing the various pairwise magnetic exchange interactions in **1**.

Due to the low symmetry of the present cluster the explicit form of the Hamiltonian is given by eqn. (1)

$$H = -2J_1(S_2 \cdot S_3 + S_3 \cdot S_4 + S_4 \cdot S_5 + S_5 \cdot S_2) - 2J_3 S_3 \cdot S_5 - 2J_2 S_2 \cdot S_4 - 2J_4 S_1 (S_2 + S_4) - 2J_5 S_1 (S_3 + S_5) \qquad (1)$$

where J_1, J_2, J_3, J_4 and J_5 correspond to the five types of exchange interactions (according to the numbering scheme shown in Fig. 3), and S_1, S_2, S_3, S_4 and S_5 are the spin operators associated with the $\mathrm{Ni^{II}}$ atoms. In an attempt to solve this Hamiltonian, a new method, simpler than that of Belorizky,[13] was applied to obtain the energies of the different spin states and, subsequently, a close expression of the magnetic susceptibility. Particularly, by using the method of hierarchy of algebras,[14] which diagonalizes the isotropic Hamiltonian of non-symmetrical molecules, we get the final analytical form for the Hamiltonian [eqn. (2)]

$$H = a_0 + a_1 C_1 + a_2 b_0^2 + a_3 (b_0 \cdot b_1) + a_4 (S_1 + b_0)^2 + a_5 (S_1 \cdot b_1) \qquad (2)$$

(where $a_0 = 4J_3 + 4J_2 + J_4 + J_5$; $a_1 = -1/4 J_3 - 1/4 J_2 + 1/2 J_1$; $a_2 = -J_1 + 1/2 J_4 + 1/2 J_5$; $a_3 = -1/2 J_3 + 1/2 J_2$; $a_4 = -1/2 J_4 - 1/2 J_5$; $a_5 = -J_4 + J_5$) containing Casimir operators[15] (C_1, $b_0 \cdot b_1$) or scalar products of operators. The only scalar product of the Hamiltonian affording non-diagonal elements is the last term, which can be treated through perturbation techniques since the a_5 coefficient is expected to be very small compared to the others. By assuming that the spectroscopic splitting constant, g, for all the individual $\mathrm{Ni^{II}}$ ions is the same and that zero-field splitting and intercluster exchange is negligible and by fixing the temperature-independent paramagnetism, $N\alpha$, at 400×10^{-6} cm^3 mol^{-1} an excellent fit§ of the experimental data was obtained from the following set of parameters: $J_1 = -5.0$, $J_2 = -10.7$, $J_3 = -39.6$, $J_4 = -6.1$, $J_5 = -4.4$ cm^{-1} and $g = 2.05$, with an R value of 0.17×10^{-6} [$R = \Sigma_n (\chi_{\mathrm{exptl}} - \chi_{\mathrm{calc}})^2$].

The large Ni(3)–O–Ni(5) angle (148.6°) is consistent with the highest $J_{\mathrm{Ni \cdots Ni}}$ value of -39.6 cm^{-1} (J_3) derived for the Ni(3)···Ni(5) interaction.[16,17] Finally, CNDO calculations performed on the bridging bta$^-$ ligand afforded the bridge orbitals able to propagate the observed antiferromagnetic interaction.

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Footnotes

† Complex **1**·$4\mathrm{Me_2CO}$·$0.5\mathrm{C_6H_{14}}$ loses solvents on drying *in vacuo*, analysing satisfactorily (C, H, N) for $[\mathrm{Ni_5(OH)(bta)_5(acac)_4(H_2O)_4}]$.

‡ *Crystal data* for **1**·$4\mathrm{Me_2CO}$·$0.5\mathrm{C_6H_{14}}$: $\mathrm{C_{65}H_{88}N_{15}Ni_5O_{17}}$, $M = 1645.07$, triclinic, $P\bar{1}$, $a = 13.855(1)$, $b = 12.013(1)$, $c = 25.611(2)$ Å, $\alpha = 89.02(1)$, $\beta = 104.76(2)$, $\gamma = 111.78(1)°$, $V = 3813.3(4)$ Å^3, $F(000) = 1718$, $Z = 2$, $D_c = 1.433$ g cm^{-3}, $\lambda = 0.71070$ Å, $T = 20$ °C, $2\theta_{\max} = 46.4°$, $wR2$ [on F^2] [$R1$(on F)] $= 0.1297(0.0514)$ for 7979 unique reflections with $I > 2\sigma(I)$. The structure was solved by direct methods using SHELXS-86 (G. M. Sheldrick, University of Göttingen, Germany 1986) and refined by full-matrix least-squares techniques using SHELXL-93 (G. M. Sheldrick, University of Göttingen, Germany 1993). All non-hydrogen atoms, with the exception of those of *n*-hexane, were refined with anisotropic thermal parameters.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

§ At first we considered three parameters within the cluster, namely J_1, J_2 and J_3 (with $J_4 = J_5 = 0$) and the best fit was made for a high negative intracluster parameter value (J_3) and two lower negative ones (J_1 and J_2) without any correlation between them. Then we kept these J_1, J_2 and J_3 values constant and fitted on J_4 and J_5. This procedure was continued until self-consistent values for all parameters were found. The same procedure was repeated next, but with J_4 and J_5 as variables and $J_1 = J_2 = J_3 = 0$ affording a new set of J parameters identical to that of the former procedure. Moreover, a series of routines (SIMPLEX) and algorithms [*e.g.* BFGS (Broyden–Fletcher–Goldfarb–Shanno) and DFP (Davidson–Fletcher–Powell)], were employed in the fitting procedure by using the multi-dimensional minimization package MERLIN/MCL.[18] In order to avoid correlations between the free J parameters, we used the RANDOM option which is a random walk in the space of parameters with volume exclusion option and line search.

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