To prepare cylindrical micelles, triblock copolymer (100 mg) was dissolved in THF (≈2 mL), the THF was evaporated and the sample dried at 85 °C for 2 h. Methanol (50 mL) was added to redisperse the polymer.

To prepare nanotubes, ozone generated (Welsback generator) was bubbled into a nanofiber solution in CH_2Cl_2 at $-78\,^{\circ}C$ for 10 min. Excess ozone was purged with nitrogen. An excess of trimethylphosphite was added and the mixture was stirred for 3 h at $-78\,^{\circ}C$ to reduce the ozonides formed to low molar mass aldehyde or ketone groups.[43]

TEM images were obtained using a Hitachi-7000 instrument operated at 100 kV. TEM specimens were prepared by aspirating a liquid sample onto a carbon-coated Cu grid and staining with OsO_4 or RuO_4. For staining P*t*BA with $(CH_3)_3SiI$, nanofibers of **1′** were mixed with a 0.14 M $(CH_3)_3SiI$ solution in CH_2Cl_2 for 1 h, followed by aspirating onto a carbon-coated copper grid. Excess $(CH_3)_3SiI$ was removed with a drop of dry CH_2Cl_2 and adsorption onto tissue.

For RB impregnation, nanotubes or nanofibers (40 mg) were mixed with RB (470 mg) and methanol (6 mL). The mixture was refluxed for 24 h. Then the methanol was evaporated. The remaining solid was suspended in water, filtered, and washed repeatedly with hot water before drying. The dried RB-loaded nanotube or nanofiber aggregates were ground with KBr for FTIR measurements.

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A Dicubane-Like Tetrameric Nickel(II) Azido Complex[**]

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Over the last few years, considerable research has been directed at the preparation of molecule-based magnets, especially nanoscale magnets in which each microcrystal behaves as a single domain. A method of preparing nanomagnets involves single molecules having ground electronic states with a large number of unpaired electrons.[1] A variety of blocking organic ligands has been used for the preparation of these cluster compounds, most of which provide oxo bridges between metal centers.[2]

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An efficient way to generate interactions between metal centers involves the use of pseudohalide ligands, among which the azide anion is one of the most interesting mediators of molecular magnetism.[3] A large number of compounds with this ligand, from dimers to three-dimensional networks, have been characterized so far.[4–12] Since the azido ligand can mediate antiferromagnetic interactions when it bridges end-to-end[10] and ferromagnetic interactions when it bridges end-on,[6, 9, 13] this variety of molecular architectures gives rise to a broad range of magnetic couplings. Antiferro- or ferromagnetic, alternating (even in the sign), and canted systems have been obtained. In the case of the very scarce cubane-like systems, those exhibiting μ-1,1-azido bridges are ferromagnetic.[8]

As mentioned above, in most of the clusters for nanomagnets the intermetallic connections are oxo bridges. The di-2-pyridylketone (dpk) ligand has been extensively used as a blocking ligand as it has three potential donor sites (the two pyridyl N atoms and the O atom of the carbonyl group) which give rise to different coordination modes.[14] Additionally, this ligand occasionally undergoes metal-promoted hydration to give a *gem*-diol,[15] which can coordinate in protonated or deprotonated form. Solvolysis reactions could be expected with other solvents and would widen the range of structural arrangements. The simultaneous use of dpk and azide ligands might enhance the formation of intermetallic bridges. Here we report on a ferromagnetic tetranuclear complex **1**, the structure of which can be described as a dicubane unit with two missing vertices.

$[\{Ni_2(dpkOH)(dpkOCH_3)(N_3)(H_2O)\}_2](ClO_4)_2 \cdot 2H_2O$ **1**

The X-ray crystal structure of **1** (Figure 1)[16] consists of centrosymmetric tetranuclear units in which the nickel(II) ions are connected by the ligands N_3, dpkOH, and dpkOCH$_3$ (dpkOH and dpkOCH$_3$ result from solvolysis of the dpk ligand) to give a face-shared dicubane-like core with two missing vertices. The Ni^{II} ions exhibit a slightly distorted octahedral [NiN$_3$O$_3$] environment, in which the Ni–N distances range from 2.024(6) (dpk) to 2.110(4) Å (N_3), and the Ni–O distances from 2.014(5) to 2.124(5) Å. The end-on azido bridges have N-Ni-N angles of 101.8(2)°, and the Ni-O-Ni angles range from 94.7(2) to 100.6(2)°. The Ni ··· Ni distance for the combination of azido and oxo bridges is 3.248(2) Å, while those for doubly oxo-bridged Ni atoms are 3.054(1) and 3.133(2) Å.

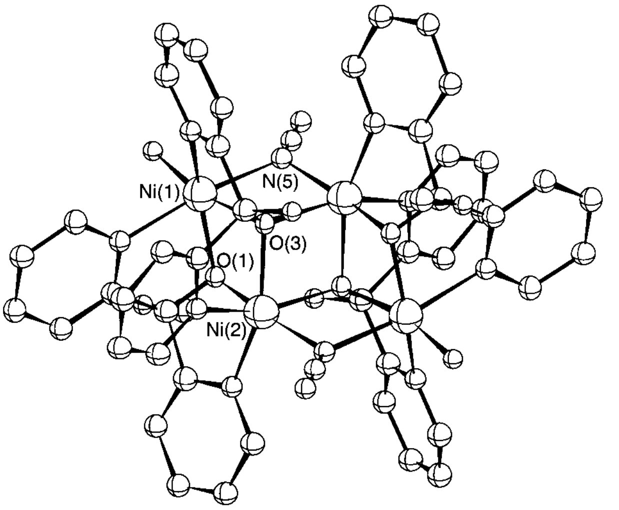

Figure 1. Molecular structure of **1** (H atoms omitted for clarity). Selected bond lengths [Å] and angles [°]: Ni(1)–N(5) 2.110(7), Ni(1)–O(1) 2.032(5), Ni(1)–O(3) 2.124(5), Ni(2a)–N(5) 2.076(6), Ni(2)–O(1) 2.120(5), Ni(2)–O(3) 2.014(5); Ni(1)-N(5)-Ni(2a) 101.8(3), Ni(1)-O(1)-Ni(2) 94.7(2), Ni(1)-O(3)-Ni(2) 95.1(2), Ni(1)-O(3)-Ni(2a) 99.2(2); symmetry code (a): $-x, -y, -z$.

The variation of the molar magnetic susceptibility χ_m was investigated for **1** in the temperature range 1.8–300 K. The product $\chi_m T$ continuously increases with decreasing temperature from 2.6 cm^3 mol^{-1} K (room temperature) to a maximum of 5.35 cm^3 mol^{-1} K at 12 K, after which $\chi_m T$ rapidly decreases and tends to zero (Figure 2). This behavior is characteristic of a system with ferromagnetic interactions. The sudden decrease in $\chi_m T$ is associated with the characteristic zero-field splitting (ZFS) of the Ni^{II} ion (intermolecular interactions are zero or negligible because the tetranuclear units are isolated by the ClO$_4^-$ counterions). For this case, where four different J values exist, an analytical expression is not available. However, the eigenvalues of the spin states can be obtained in numerical form from a full-matrix diagonalization[17] of the Hamiltonian [Eq. (1)].

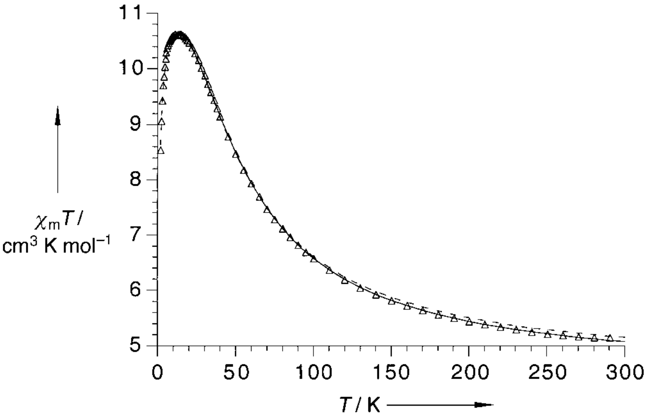

Figure 2. Temperature dependence of $\chi_m T$ for **1**. The solid line corresponds to the best fit (see text) with four different J values, the dashed line corresponds to the fit with J_A, J_B, and D.

$$\boldsymbol{H} = -J_1(S_1S_2 + S_3S_4) - J_2(S_2S_3 + S_4S_1) - J_3(S_2S_4) - J_4(S_1S_3) \quad (1)$$

The numbering of the spins follows the numbering of the nickel atoms in Figure 3 (J_4 correlates the atoms 1 and 3). The best-fit parameters[17] obtained for values up to the maximum in the $\chi_m T$ curve were $J_1 = 18.0$, $J_2 = 15.3$, $J_3 = 27.1$, $J_4 = -1.6$ cm^{-1}, $g = 2.1$ with $R = 6.4 \times 10^{-5}$ (solid line in Figure 2). Due to the similarity of the J_1 and J_2 values, the approximations $J_1 = J_2 = J_A$, $J_3 = J_B$, and $J_4 = 0$ can be made to fit the experimental data to the coupling constants and to take into account the effect of the ZFS of the $S = 4$ ground state that was observed in the $\chi_m T$ curve at low temperature. Then the

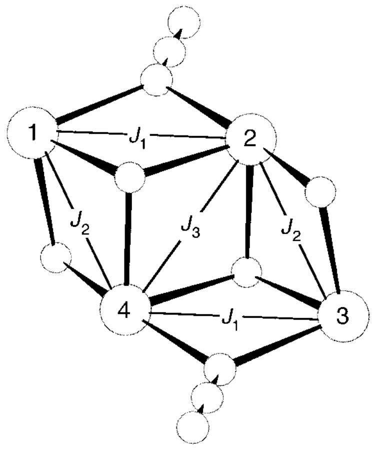

Figure 3. Coupling pattern of the four Ni atoms in **1**.

Hamiltonian reduces to Equation (2). The best-fit parameters obtained in this case were $J_A = 14.7$, $J_B = 29.1\ \text{cm}^{-1}$, $D = -0.068\ \text{cm}^{-1}$, $g = 2.12$ with $R = 2.8 \times 10^{-5}$ (dashed line in Figure 2).

$$\boldsymbol{H} = -J_A(S_1S_2 + S_3S_4 + S_2S_3 + S_4S_1) - J_B(S_2S_4) - D[S_z^2 - S(S+1)/3] \qquad (2)$$

We investigated the variation of the magnetization M with the applied magnetic field H for **1** in the range 0–7 T at 5 K (Figure 4). The magnetization reaches the saturation value expected for a tetranuclear ferromagnetic nickel(II) compound, that is, $N\beta g/2$ (≈ 8). The magnetic behavior of **1** can be explained by the existence of end-on azido bridges with angles close to 100°, which give rise to moderately strong ferromagnetic interactions that are added to the ferromagnetic interactions associated with the oxo bridges. Otherwise, the two ferromagnetically coupled μ-azido,μ-oxo Ni_2 units would couple antiferromagnetically to give $S = 0$, irrespective of the relative magnitude of the different J values.

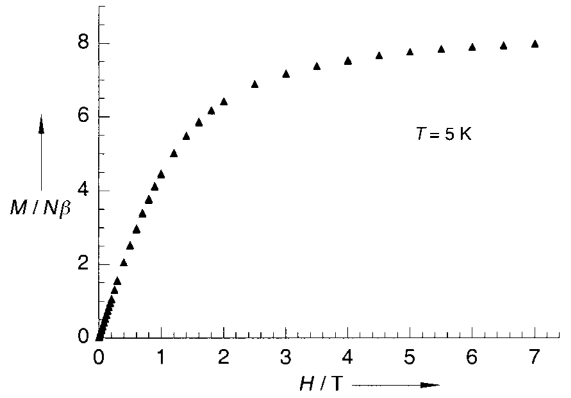

Figure 4. Field dependence of the magnetization M at 5 K for **1**.

The combination of dpk and azido ligands is a good strategy for obtaining "cubane-like" systems. The resulting compound **1** has an unusual tetranuclear dicubane-type molecular structure. The bridging ligands connecting the nickel(II) ions provide global ferromagnetic exchange interactions.

Experimental Section

Caution: Azido and perchlorate complexes of metal ions are potentially explosive. Only a small amount of material should be prepared and it should be handled with care.

Compound **1** was synthesized by slow addition of a methanolic solution (25 mL) of dpk (0.184 g, 1 mmol) to an aqueous/methanolic solution (25 mL) prepared by mixing $Ni(ClO_4)_2 \cdot 6H_2O$ (0.366 g, 1 mmol) and NaN_3 (0.065 g, 1 mmol). The reaction was carried out with continuous stirring at 45 °C. Green prismatic crystals appeared after allowing the resulting solution to stand at room temperature for two weeks. Yield: 0.220 g (62 % based on nickel); elemental analysis calcd for $C_{23}H_{24}N_7O_{10}ClNi_2$: Ni 16.5, N 13.8, C 38.8, H 3.4; found: Ni 16.7, N 14.1, C 38.9, H 3.5; IR (KBr pellet): $\tilde{\nu}$ [cm^{-1}]: 2200 (s, $\nu_{as}(N_3)$), 1328 (w, $\nu_s(N_3)$), 1610 (s, ν(CO)), 1540 (w, pyridyl stretch), 1020 (m, pyridyl breathing), 757 (m, pyridyl C–H), 1098–1125 (m, $\nu_3(ClO_4)$), 630 (s, $\nu_4(ClO_4)$); UV/Vis diffuse reflectance spectrum: $\tilde{\nu}$ [cm^{-1}]): 9520 (ν_1), 15380 (ν_2), 25000 (ν_3) from $^3A_{2g}$ to $^3T_{2g}$, $^3T_{1g}(F)$, and $^3T_{1g}(P)$, respectively.

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[16] X-ray structure analysis: Enraf-Nonius CAD-4 diffractometer. Unit cell parameters were determined from automatic centering of 25 reflections ($4 < 2\theta < 60°$) and refined by least-squares methods. Data were collected with graphite-monochromatized $Mo_{K\alpha}$ radiation ($\lambda = 0.71069$ Å) by using the ω scan technique. Lorentzian, polarization, and extinction corrections were made. The structure was solved by direct methods and successive Fourier difference syntheses with the SHELXL-93 computing program. Crystal data for **1**: $C_{23}H_{24}ClN_7Ni_2O_{10}$ ($M_r = 711.36$), monoclinic, space group $P2_1/c$, $a = 13.456(3)$, $b = 10.906(2)$, $c = 19.990(7)$ Å, $\beta = 91.59(3)$, $V = 2932.4(13)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.611$ g cm^{-3}, $\mu = 14.40$ cm^{-1}, $F(000) = 1456$. The refinements by full-matrix least-squares methods gave final $R1(F_o) = 0.074$, $wR2(F_o^2) = 0.184$ and $S = 0.999$ for 7643 reflections with $I \geq 2\sigma(I)$ and 389 variables. All non-hydrogen atoms were refined anisotropically. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-102206. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[17] The calculations were made with the computer program CLUMAG, which uses the irreducible tensor operator formalism (ITO): D. Gatteschi, L. Pardi, *Gazz. Chim. Ital.* **1993**, *123*, 231.

5-(*β*-Cyclodextrinylamino)-5-Deoxy-*α*-D-Riboses as Models for Nuclease, Ligase, Phosphatase, and Phosphorylase[**]

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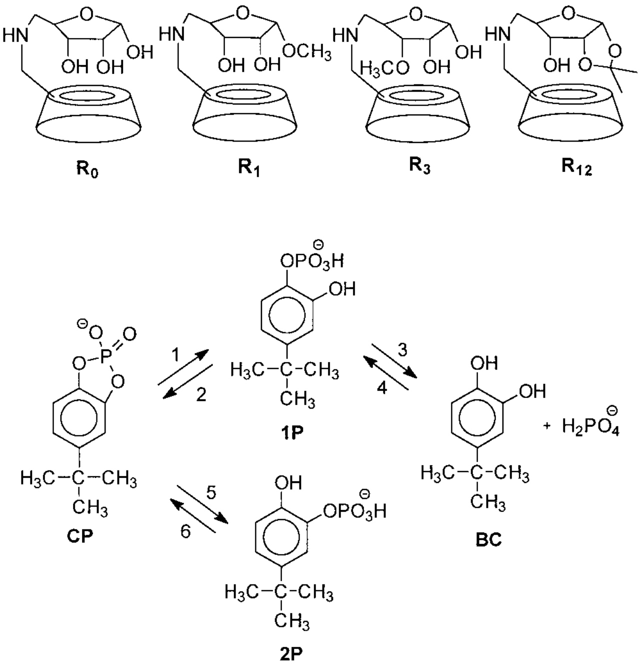
The synthesis and activity testing of enzyme models have drawn attention to the elucidation of enzyme structures and mechanisms.[1] Several models have been synthesized and their activities have been tested for nuclease, ligase, phosphatase, and phosphorylase.[2] We recently reported that ribose-containing polymers show catalytic activity for the cleavage of DNA.[3] The study of various polymer structures strongly suggested that the *vic-cis*-diol groups of the ribose rings play a key role in the catalysis, which is surprising because there are plenty of biopolymers containing ribose rings. This prompted us to further study the mechanism of action by synthesizing enzyme models containing riboses capping *β*-cyclodextrin (CD) and then performing model reactions with phosphate substrates. The models showed catalytic activity for the hydrolysis of phosphodiester (nuclease activity), the hydrolysis of phosphomonoester (phosphatase activity), the esterification of phosphomonoester to phosphate diester (ligase activity), and the phosphorylation of alcohols with phosphate ions (phosphorylase activity).

6-Monotosyl-*β*-cyclodextrin was prepared as described in the literature.[4] It was treated with 5-amino-5-deoxy-1,2-*O*-isopropylidene-*α*-D-ribose to yield 5-(*β*-cyclodextrinylamino)-5-deoxy-1,2-*O*-isopropylidene-*α*-D-ribose (**R$_{12}$**), which was hydrolyzed to form 5-(*β*-cyclodextrinylamino)-5-deoxy-*α*-D-ribose (**R$_0$**) (Scheme 1). The derivatives **R$_1$** and **R$_3$**, in which 1-OH and 3-OH of the ribose ring are blocked by methyl groups, were synthesized by similar methods.[5] The *N*-methylpyridinium salt of the cyclic phosphate (**CP**)[5] and the 1-phosphate (**1P**) and 2-phosphate (**2P**) of 4-*tert*-butylcatechol (**BC**) were also synthesized as substrates (Scheme 1). Compounds **BC**[6] and **CP** are well known to form inclusion complexes with CD, and CD capped with imidazole has been investigated as a nuclease model using **CP** as substrate.[2]



Scheme 1. *β*-Cyclodextrinyl compounds and reactions of phosphate esters.

Reactions 1 (and 5), 2, 3, and 4 (Scheme 1) are the model reactions for nuclease, ligase, phosphatase, and phosphorylase, respectively. The rates of the reactions were measured at pH 7.4 (Tris buffer), ionic strength (μ) of 0.2 (KCl), and 25 °C by HPLC in the presence of the cyclodextrinyl compounds (4 mM) and the substrates (0.4 mM). This concentration ratio was chosen for the activity measurements since no significant rate acceleration was observed by further increasing the concentration of the former compound.

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