(0.170 g, 52 % yield). Elemental analysis calcd (%) for $C_{28}H_{44}O_{14}NKTi$: C 47.66, H 6.28, N 1.99; found: C 47.43, H 6.27, N 2.06; m.p. 124–125 °C (decomp); IR (THF): $\tilde{\nu} = 1930$ (m), 1793 cm^{-1} (s) (CO); ^{1}H NMR (300 MHz, [D$_8$]THF, 0 °C, TMS): $\delta = 6.16$ (m, 2H, pyrrolyl), 5.40 (m, 2H, pyrrolyl), 3.62 (s, 40H, [15]crown-5); ^{13}C{^{1}H}(75 MHz, [D$_8$]THF, 0 °C, TMS): $\delta = 289$ (s, CO), 114 (s, pyrrolyl), 99 (s, pyrrolyl), 69 (s, [15]crown-5).

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A Metamagnetic Two-Dimensional Molecular Material with Nickel(II) and Azide[**]

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Until a few years ago, the main aim of magnetochemical research was to show that molecular magnetism could lead to the development of new magnetic materials.[1] One strategy for the design of molecular-based magnets involves assembling transition metal ions in one-, two-, or three-dimensional networks. We are currently studying materials formed from the interaction of transition metal ions with the azido ligand. The azido bridge is a versatile and efficient magnetic coupler; it may transmit either antiferro- or ferromagnetic interactions. Working with Ni^{II} salts and diamines as blocking ligands, for a Ni/diamine ratio of 1/1 four positions in the coordination sphere of the nickel are free. These positions can be occupied by four azido bridges. The most remarkable species obtained to date are the neutral polymeric compounds $[Ni(\mu\text{-}N_3)_2\text{-}(diamine)]_n$: three one-dimensional systems showing global ferromagnetic behavior and metamagnetism at low temperature,[2] five one-dimensional complexes with alternating end-on (EO) and end-to-end (EE) azido bridges in different sequences showing global anti-ferromagnetic behavior,[3–6]

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and one two-dimensional sheet showing global antiferromagnetic behavior and a canting phenomenon at low temperature (50 K) that gives the complex the characteristics of a molecular magnet.[7] Here, we report the synthesis, structure, and magnetic properties of $[Ni(\mu\text{-}N_3)_2(N,N\text{-}Et_2\text{-}N'\text{-}Me\text{-}en)]_n$ (**1**; N,N-Et_2-N'-Me-en = N,N-diethyl-N'-methylethylenediamine), which is the first example of a metamagnetic two-dimensional molecular material with Ni^{II} and azide, featuring short-range, intralayer, ferromagnetic behavior and weak interlayer antiferromagnetic interactions. The crystal structure analysis[8] reveals parallel sheets of nickel atoms linked by EO and EE azido bridges (Figure 1). Each nickel atom is in a distorted octahedral NiN_6 environment and is linked to three other nickel atoms: through two EO azido bridges to one nickel atom and through two EE bridges in a *cis* position to two nickel atoms. Each Ni^{II} ion completes its coordination by binding one bidentate N,N-Et_2-N'-Me-en ligand. The Ni–N bond lengths range between 2.09 and 2.15 Å, which is characteristic of these complexes. The Ni-N-Ni angle of 100.46° lies within the range of reported values.[2, 4, 5] All the EE fragments are equivalent and the coordination of the azido bridge is asymmetric; the two Ni-N-N angles are 136.9° and 144.2°, and the Ni-N_3-Ni torsion angle is 110.44°.

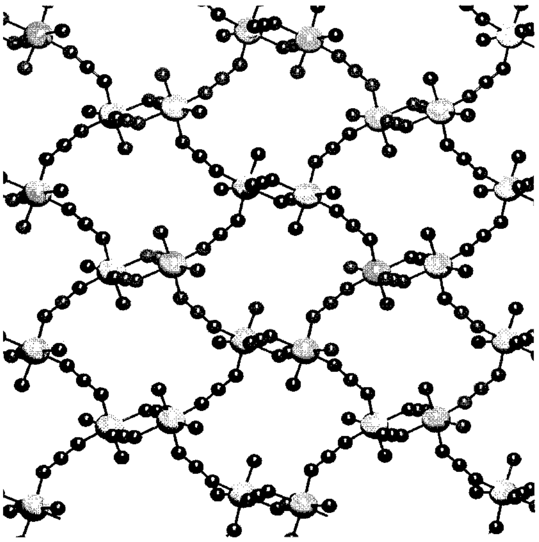

Figure 1. Layer structure of **1**. Dinuclear nickel units, bridged by two EO azido bridges, are linked to four equivalent units by means of four single EE azido bridges. For clarity, only the N atoms of the amine ligands are shown.

The cryomagnetic behavior of **1** is shown in Figure 2. At room temperature $\chi_M T$ is the same ($1.44\ cm^3 K mol^{-1}$) for all values of the applied field. This value increases monotonically with cooling to 60 K. As the temperature is lowered further $\chi_M T$ increases more and more rapidly, reaching a maximum value around 16 K, before decreasing at lower temperatures. The maximum value of $\chi_M T$ is field dependent, but the temperature for the maximum $\chi_M T$ remains unchanged. The magnetic behavior, except for the decreasing $\chi_M T$ below 16 K, suggests an intramolecular ferromagnetic interaction between adjacent Ni^{II} ions. These results can be explained by considering the structure. The interaction between the nickel atoms through the EO azido bridges, according to the structural parameters and literature data, [9, 10] must be ferromagnetic. For the interaction through the EE azido ligand, previous studies[11, 12] show that the value of the superexchange coupling depends mainly on the Ni-N-N angle α and on the Ni-N_3-Ni torsion angle θ. Considering the Ni-N-N angle, the maximum antiferromagnetic coupling would be expected for $\alpha = 108°$. For greater values, the interaction must decrease and reach accidental orthogonality at $\alpha = 165°$. Taking into account the torsion angle, the maximum superexchange is found for $\theta = 180°$ or 0° and diminishes gradually to an expected minimum of zero for a torsion angle of $\theta = 90°$. To our knowledge all compounds with an EE azido bridge and a Ni^{II} ion are antiferromagnetic with the exception of two compounds: one is a dinuclear nickel(II) cryptate,[13] in which the Ni-N-N angles are 165.8° and 157.6°; the other is a one-dimensional compound,[14] in which the torsion angle is 75.7°. For **1** the values of the Ni-N-N angles deviate from 108°, and the torsion angle is close to 90°, in the range where the antiferromagnetic contribution is minimized to favor the ferromagnetic contribution.

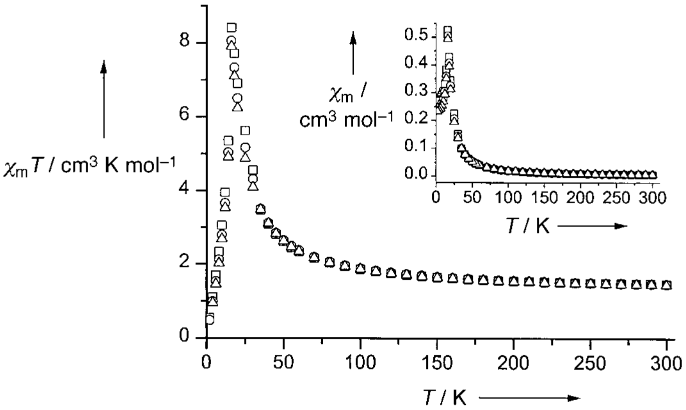

Figure 2. Plot of $\chi_M T$ versus temperature at three values of the applied field (□: 500 G, ○: 1000 G, △: 2000 G). Inset: Plot of χ_M versus temperature.

The magnetic behavior of **1**, with the abrupt increase in the value of $\chi_M T$ on cooling, a maximum around 16 K, and decreasing $\chi_M T$ below this temperature, suggests a three-dimensional antiferromagnetic ordering of the ferromagnetic layers.[15] Further support for this comes from magnetization versus applied field plots at three temperatures (Figure 3). All curves have the sigmoidal shape (more markedly at lower temperatures) expected for a metamagnet: initially the magnetization increases slightly with increasing field strength because of antiferromagnetic interlayer interactions, subsequently it increases abruptly for a phase transition to a ferromagnetic state, and finally it reaches a saturation magnetization plateau.

The magnetization was also measured in the range of 3–20 K (Figure 4). The field-cooled magnetization (FCM), measured under an applied field of 10 G, increases rapidly on cooling to 16 K and then diminishes. This behavior is typical of metamagnetic ordering. When the applied field was switched off at 3 K, there remained a remnant magnetization (RM), that decreased upon warming. The zero-field-cooled magnetization (ZFCM), measured upon warming under an

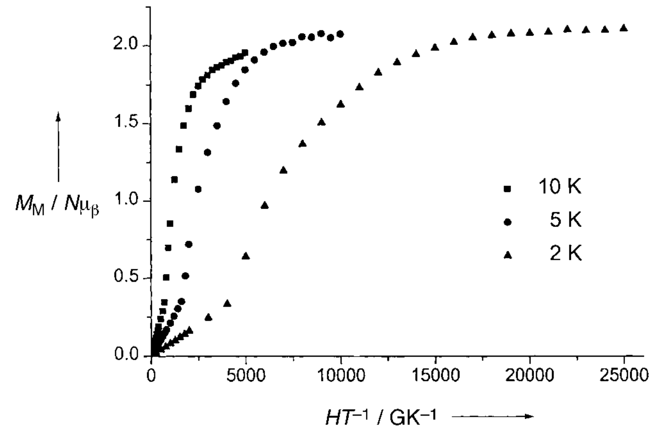

Figure 3. Magnetization versus applied field at three temperatures.

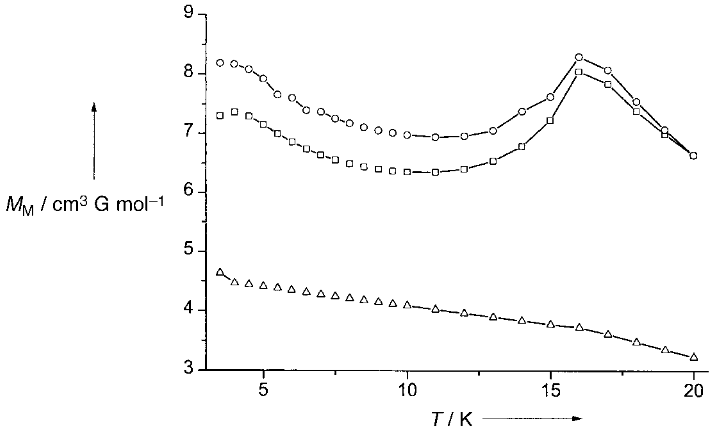

Figure 4. Plots of FCM (○), ZFCM (□), and RM (△) versus temperature at an applied field of 10 G.

applied field of 10 G, shows a maximum at 16 K and decreases rapidly as the temperature is increased further.

The present example is a new demonstration of the versatility of the azido bridge for building molecular-based materials. The magnetic measurement shows, for the first time in a Ni^{II} azido compound, an intralayer ferromagnetic interaction. Finally, the interlayer antiferromagnetic interaction gives rise to metamagnetic behavior. In order to complete the magnetic studies, measurements at alternating current, and of the FCM at different field strengths are now in progress.

Experimental Section

A solution of *N*,*N*-Et_2-*N*′-Me-en (0.26 g, 2 mmol) in DMF/EtOH (1/1, 10 mL) was added to a solution of $Ni(NO_3)_2 \cdot 6H_2O$ (0.58 g, 2 mmol) in DMF/EtOH (20 mL). Solid NaN_3 (0.26 g, 2 mmol) was added slowly. The clear dark green solution was filtered to remove any impurities and left to stand undisturbed at room temperature. Single green crystals of **1** were collected after two weeks.

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