Low-dimensional magnetic compounds, especially zero-dimensional magnetic clusters and 1D chain compounds that show single-molecule[1,2] and single-chain[3] magnetic properties, are currently of ongoing interest for the design and synthesis of new molecule-based magnets. Well-documented examples include Mn$_{12}$[4] and Fe$_8$[5] for single-molecule magnets (SMMs), and [Co(hfacac)$_2$(NITPhOMe)] (hfacac = hexafluoroacetylacetone, NITPhOMe = 4’-methoxyphenyl-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide)[6] and [Mn$_6$(saltsmen)$_2$, Ni(pao)$_2$L$_2$(A)$_2$ (saltsmen = 2,2’-dimethylformamide) that contains isolated 1D Ni$^2+$ chains bridged by the magnetic hysteresis loops even at 10 K.}

In order to obtain a magnetic ground-state for a chain, individual magnetic moments cannot cancel out. This condition can be satisfied if the chain is ferromagnetic (e.g., [FeL(CN)$_2$Co(H$_2$O)$_2$] (L = 2,2’-bipyridine or 1,10-phenanthroline, x = 1 or 2), and [Co(bt)(N$_3$)$_2$] (bt = 2,2’-bithiazoline)[7] or ferrimagnetic, such as [Co(hfacac)$_2$(NITPhOMe)].[8] There is another way to achieve this goal in an antiferromagnetic chain: the spin-canting that arises from the non-colinear spin arrangements because of the existence of an antisymmetrical component of the superexchange interaction (Dzyaloshinskii–Moriya interaction, DMI) or the appropriate anisotropy.[8] Such is the case in the reported SCM of Co(H$_2$L)(H$_2$O) (H$_2$L = 4-Me-C$_4$H$_2$CH$_2$N(CH$_2$PO$_3$H$_2$)$_2$).[9]

In this paper, the X-ray structure and magnetic properties of a new compound [Ni(u-N$_3$)(bmdt)(N$_3$)]$_2$(DMF)$_n$ (I) (bmdt = N,N’-bis(4-methoxybenzyl)-diethylenetriamine, DMF = N,N-dimethylformamide) that contains isolated 1D Ni$^{2+}$ chains bridged by a single end-to-end (EE) azide is reported. Strong antiferromagnetic coupling and spin-canting are observed between the adjacent Ni$^{2+}$ ions. The unexhausted magnetic moment in the chain leads to a weak ferromagnetic behavior with slow relaxation similar to a single chain magnet: strong frequency dependence of AC susceptibility and the existence of the magnetic hysteresis loops even at 10 K.

The structure of I contains infinite 1D Ni$^{2+}$ chains bridged by single EE N$_3^-$ with isolated solvent DMF molecules among the chains (Fig. 1). There is only one unique Ni$^{2+}$ ion in the structure, coordinated by six nitrogen atoms, three of which are from the ligand bmdt and the rest from two bridging trans azides and one terminal azide. The coordination environment of Ni can be considered as a tetragonally compressed octahedron since the two axial Ni–N bond lengths for Ni1–N2 (2.08 Å) and Ni1–N4 (2.07 Å) are shorter than those of the four equatorial bonds (2.11–2.16 Å). The tridentate ligand bmdt chelates to the Ni$^{2+}$ ion with its three amido N atoms, with the two 4-methoxybenzyl groups on both sides of the chain. Bridged by the EE azide, the Ni$^{2+}$ ions form an equally spaced 1D magnetic chain along the b direction with an Ni–Ni distance of 5.60 Å (Fig. 1a).

The Ni1–N9 and Ni2–N7 lengths are 2.13 and 2.11 Å. The Ni1–N9 and Ni2–N7–N8 angles are 33.8° and 34.3°, respectively. The structure of I also exhibits a weak ferromagnetic behavior with slow relaxation similar to a single chain magnet: strong frequency dependence of AC susceptibility and the existence of the magnetic hysteresis loops even at 10 K.

**Communication**

**Weak Ferromagnetism and Dynamic Magnetic Behavior in a Single End-to-End Azide-Bridged Nickel(II) Chain**

By Xue-Ting Liu,* Xin-Yi Wang, Wei-Xin Zhang, Peng Cui, and Song Gao*
The temperature ($T$) dependence of the molar magnetic susceptibility ($\chi_m$) of a collection of polycrystalline samples of 1 under 1 kOe (1 Oe = 79.58 A m$^{-1}$) from 2 to 300 K is shown in Figure 2a as $\chi_mT$ versus $T$. At 300 K the $\chi_mT$ is 1.21 cm$^3$ mol$^{-1}$ K, which is slightly larger than the spin-only value of 1.00 cm$^3$ mol$^{-1}$ K for one Ni$^{2+}$ ion with spin number $S=1$ and a Lande factor $g=2.00$, indicating a possible orbital contribution. At high temperatures above 80 K, the $\chi_mT$ decreases slightly with decreasing temperature to reach a minimum (0.98 cm$^3$ mol$^{-1}$ K), and then increases to a peak of 5.30 cm$^3$ mol$^{-1}$ K at 24 K, followed by a drop down to 0.23 cm$^3$ mol$^{-1}$ K at 2 K. This behavior is reminiscent of a ferrimagnet or a system of spin-canting. Fitting the data above 150 K with the Curie–Weiss law gives the Curie constant $C=1.43$ cm$^3$ mol$^{-1}$ K and Weiss constant $\theta=-58$ K. This large negative $\theta$ value clearly indicates the occurrence of efficient antiferromagnetic coupling between the Ni$^{2+}$ ions, although it might partly come from spin-orbital coupling. Considering the isolated 1D equally spaced chain structure, the $\chi_mT$ value can be fitted above 100 K with the analytical expression for an antiferromagnetic chain of $S=1$ developed by Weng and others[8,10] with the Hamiltonian expression

$$H = -J \sum_{i<j} S_i S_j,$$

(1)

where $x = \left| J/\mu_B k_B T \right|$, $J$ is the coupling of the neighboring Ni$^{2+}$ bridged by an EE azide ($J > 0$ for ferromagnetic and $J < 0$ for antiferromagnetic coupling), $N_A$ is Avogadro’s number, and $k_B$ is the Boltzmann constant. The best fit (black line in Fig. 2a) gives $J = -16.0(7)$ cm$^{-1}$ and $g = 2.30(1)$ with $R = 1.6 \times 10^{-4} [R = \chi_{\text{calc}} T - \chi_{\text{obs}} T]^2]$. On the other hand, to investigate the ferromagnetic-like behavior, the experimental data can be fitted down to 30 K using the non-critical-scaling theory with the following simple phenomenological equation[11]

$$\chi_m T = C_1 \exp(a J/k_B T) + C_2 \exp(b J/k_B T)$$

(2)

where $a J < 0$ indicates the antiferromagnetic interaction within the chain, which is responsible for the initial high temperature decay of $\chi_m T$. $b J > 0$ denotes the ferromagnetic-like interaction, which leads to the increase of $\chi_m T$ below 80 K. $C_1 + C_2$ roughly equals the Curie constant at high temperatures. The best fit (the gray line and the dashed lines in Fig. 2a) gives $C_1 = 1.27$, $a J = -40.5$ cm$^{-1}$, $C_2 = 0.091$, and $b J = 79.2$ cm$^{-1}$.  

Figure 1. a) View of the 1D chain structure of 1 along the $b$ axis. The intrachain Ni–Ni distance is 5.602 Å. b) Crystal packing in the ac plane. The shortest interchain distances are labeled in the graph. DMF is omitted for clarity.
To further investigate the possible phase transition suggested by the hump of the $\chi_m T$ curve, the zero-field-cooled magnetization (ZFCM) and field-cooled magnetization (FCM) are measured from 2 to 50 K under 20 Oe. As can be seen from the inset of Figure 2a, the ZFCM shows a peak at 14 K and diverges from the FCM at about 15.5 K. This kind of divergence reveals a possible transition from a paramagnetic state to either a long-range ordered, a spin-glass, or a superparamagnetic state. The isothermal magnetization $M(H)$ at 1.8 K with a field of up to 50 kOe and hysteresis loops at 1.8, 5.2, 10, and 15 K have been measured and are represented in Figure S1 (Supporting Information) and Figure 2b. At 1.8 K, the initial magnetization increases linearly with field up to about 5 kOe, and then increases abruptly up to 10 kOe, followed by a slow increase to 0.36 $\mu_B$ ($1 \mu_B = 9.27402 \times 10^{-24} \text{ Am}^2$) per Ni$^{2+}$ at 50 kOe, which is far from the saturated magnetization value $M_S = 2 \mu_B$ for a Ni$^{2+}$ ion (assuming $g = 2$). A hysteresis loop can be clearly seen even at 10 K. The coercivity fields and the remnant magnetizations are $H_C = 4.37$, 3.45, and 0.61 kOe, $M_R = 0.066$, 0.064, and 0.042 $\mu_B$ ($\mu_B =$ Bohr magneton), at 1.8, 5.2, and 10 K, respectively. The large departure from saturation of the $M(H)$ curve and the observation of the hysteresis loops are indicative of a spin-canted weak ferromagnetic state for $\text{I}$, which, as discussed in the structure description, possibly arises from DMI and the tilting of the coordination polyhedra of Ni$^{2+}$. From the remnant magnetization at 1.8 K and the equation $\sin(\alpha) = M_R / M_S$, the canting angle $\alpha$ is estimated to be about 1.9°.

Furthermore, AC susceptibility under the DC field $H_{DC} = 0$ Oe and the AC field $H_{AC} = 3$ Oe was measured from 2 to 30 K with a frequency from 1.4 to $10^4$ Hz. The results are displayed in Figure 3. Surprisingly, both the in-phase and out-of-phase signals, $\chi_m'$ and $\chi_m''$, go through a maximum with strong frequency dependence. The peak temperature ($T_p$) of $\chi_m'$ is measured by a parameter $\phi = (\Delta T_p / T_p)$. The shifts of these peak temperatures are indicative of a spin-canted weak ferromagnetic state for $\text{I}$, which, as discussed in the structure description, possibly arises from DMI and the tilting of the coordination polyhedra of Ni$^{2+}$. From the remnant magnetization at 1.8 K and the equation $\sin(\alpha) = M_R / M_S$, the canting angle $\alpha$ is estimated to be about 1.9°.

Figure 2. a) Temperature dependence of the magnetic susceptibility for $\text{I}$. The inset shows the zero-field-cooled (ZFC) and field-cooled (FC) magnetization at 20 Oe; the black line is the fit of Weng’s model; the gray line and the dashed lines correspond to the fit to a model allowing for the competition of two exponential contributions (Equation (2)). b) Hysteresis loops at different temperatures for $\text{I}$.

Figure 3. Temperature dependence of the a) real and b) imaginary components of the AC susceptibility in a zero applied static field with an oscillating field of 3 Oe in the frequency range of 1.4–9999 Hz. The lines are guides.
$$\Delta \log \beta = 0.07 \ (f \text{ is the frequency of } H_{AC}), \text{ which is in between the values of a normal spin-glass and a superparamagnet. Although the frequency dependence of } T_{f} \text{ on } \Delta \omega^{*} \text{ can be fitted well to the Arrhenius law } \tau = \tau_{0} \exp (\Delta E/k_{B} T) \ (\tau \text{ is the relaxation time, } \tau_{0} \text{ is the pre-exponential factor, and } \Delta E \text{ is the energy gap; Fig. S2a}), \text{ to give the best set of parameters } \tau_{0} = 6.3 \times 10^{-16} \ s \text{ and } \Delta E/k_{B} = 499(7) \ K, \text{ the resultant } \tau_{0} \text{ seems too small and the } \Delta E \text{ looks much higher for a typical SCF following Glauber dynamics.}^{[3,12]} \text{ Meanwhile, the same set of data can also be fitted by the conventional critical scaling law of the spin dynamics as described by } \\
\tau = \tau_{0} ((T_{F} - T_{f})/T_{f})^{-\gamma}, \\
\text{where } T_{F} = 1/(2\pi f), \text{ which gives } \tau_{0} = 1.0 \ s, \gamma = 7.3, \text{ and } T_{f} = 7.2 \ K \ (\text{Fig. S2b; } T_{f} \text{ is the freezing temperature for a spin-glass phase, } \\
\gamma \text{ is the critical exponent value). The obtained } \gamma \text{ of } 7.3 \text{ happens to fall in the range (from 4 to 12) for various spin-glasses.}^{[5]}$$

What is the real ground state of $I$? Is there long-range order? Concerning the ground state of $I$ at low temperature, the non-critical-scaling theory is applied, to check the plot of $d(\log T)/d(\log \gamma_{f})$ versus $T$ (Fig. S3). Here $\gamma_{f} = \gamma_{f}T = 1.27 \times \exp(-0.5/k_{B} T)$ describes the ferromagnetic contribution, which is obtained by subtracting the antiferromagnetic component that dominates at the high temperature regime from the total $\gamma_{f}T$. As can be seen from Figure S3, the data in the temperature window from 40 to 120 K show nearly a straight line that roughly intersects the horizontal coordinate axes at the origin. This behavior may rule out the phase transition to long-range ordering of this system above 0 K, and suggests that $I$ is indeed a real 1D system.$^{[11]}$

As shown above, the magnetic behavior of $I$ is quite unusual. Compound $I$ is tentatively ascribed to be a canted, weak ferromagnetic chain with unusual spin-glass-like dynamic relaxation. Since no structural disorder and no apparent magnetic frustration are found in $I$, it is presumed that the slow relaxation behavior might come from the movement of the domain walls,$^{[4,12]}$ although it should not be interpreted simply by the Glauber model.$^{[13]}$ A more thorough study on the unusual spin dynamics observed here is needed to fully understand the physical properties of $I$.

**Experimental**

**Preparation of [Ni$_{4}$N$_{2}$]((bmdt)$_{2}$)(N$_{3}$)$_{4}$ (DMF)$_{2}$ (I):** To an ethanol solution of bmdt·3HCl (0.181 g, 0.4 mmol; prepared by a reported method$^{[14]}$) was added NiCl$_{2}$ (0.095 g, 0.4 mmol), and then 0.2 mL of aqueous NaOH solution (0.8 mmol, 4 N). After heating to reflux for two hours, Na$_{2}$S (0.13 g, 2 mmol) was added. Two hours later, a large amount of precipitate formed. After filtration, the obtained gray solid was washed with distilled water and ethanol, respectively, and then dried under vacuum. The solid was dissolved in hot DMF. The residue was filtered off. The resulting dark-green solution was left undisturbed. Two weeks later, X-ray quality blue crystals were obtained. Yield: 0.034 g, 15%. Anal. Calc: for C$_{23}$H$_{36}$N$_{10}$NiO$_{3}$: C, 49.39; H, 6.49; N, 25.05. Found: C, 49.23; H, 6.61; N, 25.13. IR (KBr pellet, cm$^{-1}$): 3429 w, 3248 m, 3194 m, 2935 m, 2870 m, 2079 vs, 2054 vs, 1658 vs, 1612 m, 1512 s, 1454 m, 1388 w, 1303 w, 1251 s, 1180 m, 1099 w, 1035 s, 979 s, 835 m, 802 w; 756 w, 599 w, 514 w.


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