Magnetic Phase Transitions in a Ni$_4$O$_4$-Cubane-Based Metal–Organic Framework

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Abstract: An unprecedented spin cluster-based network architecture \(\{\text{Ni}^3_2(pdaa)(\text{OH})_2[H_2O]\}_n\) (\(pdaa = 1,4\)-phenylene diacetic acid), comprising 1D linear chains of \(\text{Ni}^3\) ions cross-linked via \(\text{Ni}_4\text{O}_4\) cubanes, forms under hydrothermal conditions; this 3D coordination network exhibits magnetic ordering at 23.9 K as well as a second magnetic ordering process at 2.8 K likely associated with a structural phase transition.

Introduction

Interest in molecule-based magnetic materials has greatly increased over the last decade, primarily driven by the fact that such materials can help the understanding of magneto-structural correlations and the fundamental phenomena of magnetism at the intersection of molecular to extended magnetic systems; some may even lead to applications. In addition to the nature of the metal spin centers, the bulk magnetic properties mainly depend on the bridging modes and geometries of the bridging ligands. Since the structural factors governing the exchange coupling between paramagnetic centers are complex and in part remain elusive, the pursuit of designed polynuclear complexes and extended networks with predictable magnetic properties continues to be challenging. Magnetic phenomena such as ferromagnetic, ferrimagnetic, and antiferromagnetic long-range ordering at low temperatures have been observed for many transition metal coordination compounds. In contrast, only relatively few magnetically ordered complexes exhibit magnetic phase transitions (MPTs) such as metamagnetic phase transitions. In most cases of porous extended systems displaying bulk ordering phenomena, MPTs are associated with solvation/desorvation. In order to gain bulk magnetic ordering, a strategy to connect various building blocks, that is, single-molecule magnets (SMMs) or single-chain magnets (SCMs), covalently or through cooperative van der Waals forces to fabricate 3D network materials, has recently been adopted. Meanwhile, materials showing multiple MPTs remain scarce. Cheng et al. reported a 3D nickel-organic framework that exhibits canting antiferromagnetism at 5.0 K whilst below this temperature slow relaxation was also observed. Recently, Elizabeth et al. studied an order-disorder phase transition in the cobalt-based MOF \((\text{CH}_3)_2\text{NH}_2\text{Co}(\text{CHO})_2\). This material displayed antiferromagnetic ordering below 15 K and a second magnetic transition at ca. 11 K. We herein report the first example of a \(\text{Ni}_4\text{O}_4\) cubane-based 3D network, isolated as \(\{\text{Ni}^3_2(pdaa)(\text{OH})_2[H_2O]\}_n\), that exhibits multiple magnetic phase transitions, specifically at 23.9 K and 2.8 K.

Compound 1 was hydrothermally synthesized and crystallizes in the tetragonal space group \(I\bar{4} / a\) (\(Z = 16\)). Analysis of the single-crystal X-ray diffraction data indicates two main structural features: (a) Linear chains of \(\text{Ni}^3\) atoms running perpendicular to each other (along \(a\) and \(b\), Figure 1a) that are assembled and interlinked by pdaa ligands (Figure 1b). Each chain consists of two alternating types of \(\text{Ni}^3\) chain centers (\(\text{Ni}1\) and \(\text{Ni}2\)) in the same \(\text{NiO}_2\) coordination environment, but with slightly different bond distances and angles, and separated by 3.057 Å. Each \(\text{Ni}^3\) chain site is coordinated by four \(\text{O}\) atoms belonging to four different pdaa ligands and two \(\text{O}\) atoms of two different \(\text{OH}^-\) (O6W) ions (\(\text{Ni}-\text{O}: 1.977(2)–2.172(3) \text{Å}, \text{O}-\text{Ni}-\text{O}: 80.20(10)–179.999(1)°\)), resulting in a slightly distorted octahedral geometry. (b) Distorted \(\text{Ni}_4\text{O}_4\) cubane units bridging the chains (Figure 1c). Each \(S_2\)-symmetric \(\text{Ni}_4\text{O}_4\) cubane moiety consists of one type of nickel center (\(\text{Ni}3\)), which is connected with three different oxygen atoms (\(\mu_3\)-O) of bridging OH$^-$. 

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The Ni\textsuperscript{II} center and a second oxygen atom (O5) bridges the two Ni\textsuperscript{II} centers of neighboring linear chains. The two flexible arms of the pdaa ligand are directed towards the same side and twist perpendicular to each other to coordinate to the Ni\textsuperscript{II} ions. Centers, bridged via Ni=O, cubanes, to form a 3D network (Figure 2).

**Results and Discussion**

**Magnetochemical properties**

Magnetic measurements of compound 1 in static magnetic fields are summarized in Figure 3. At 300 K and 0.1 T, $\chi_{m} T = 2.68 \text{ cm}^{3} \text{Kmol}^{-1}$ lies within the expected range of 1.96–3.06 cm$^{3}$ Kmol$^{-1}$ for two non-interacting Ni$^{II}$ centers.\[^9\] With decreasing temperature, $\chi_{m} T$ slightly increases until ca. 50 K, subsequently showing a sharp and very pronounced maximum at ca. 20 K and then dropping down to a minimum at 3.5 K, only to rise once again to 3.52 cm$^{3}$ Kmol$^{-1}$ at 2.0 K. The corresponding inverse molar magnetic susceptibility (Figure 3a, inset) is characterized by a linear behavior for most of the temperatures ($T > 20$ K), a plateau in the range from 20 to 4.5 K, and another decreasing curve below 4.5 K down to 2.0 K. Besides FC (field cooling) measurements, we additionally measured the sample at ZFC (zero field cooling), but found only marginal differences between both measurements for data below 20 K (as indicated by the marginal displacement of the data at these temperatures in Figure 3a).

While the first maximum can be unambiguously assigned to predominant ferromagnetic exchange interactions between the Ni$^{II}$ centers of 1, the subsequent occurrence of the minimum combined with the increase of $\chi_{m} T$ for the lowest temperatures could be due to impurities. We, thus, measured multiple, individually synthesized batches of 1 to find that all yielded virtually identical data. Therefore, we can, with near certain-
centers can be approximately interpreted as effective magnetic moments of 1 at low temperatures. Since octahedral Ni\(^{II}\) centers can be approximately interpreted as effective isotropic spin centers with \(S_\text{eff} = 1\), we analyzed the linear segment of the \(x_m \sim T\) vs. \(T\) curve in terms of the Curie–Weiss law \(\chi_m = C / (T - \theta_\text{W})\). The least-squares fit yields \(C = (2.595 \pm 0.003) \text{ cm}^3 \text{Kmol}^{-1}\) and \(\theta_\text{W} = (9.76 \pm 0.20) \text{ K}\). The Weiss temperature confirms the predominant ferromagnetic exchange interactions (since \(\theta_\text{W} > 0\)). In addition, we derive the (mean) effective g factor from the Curie constant as \(g_\text{eff} = (2.28 \pm 0.01)\) for each Ni\(^{II}\) center, fully in line with the expected value for an octahedrally coordinated Ni\(^{II}\) ion.

The molar magnetization \(M_m\) was studied as function of the applied external magnetic field \(B\) at 2.5 K and 4.2 K, that is, at temperatures above and below the minimum of the \(x_m \sim T\) vs. \(T\) curve, which are still small enough to result in sufficiently large magnetization values in order to detect hysteresis behavior. Both magnetization curves are similar for fields with magnitudes larger than ca. 1 T, for which they almost linearly increase up to 1.7 \(N_a\) \(\mu_0\) at 5.0 T. However, they significantly differ at fields between \(\pm 0.8\) T: At 2.5 K, the magnetization gradually approaches a value of ca. \(\pm 0.1\) \(N_a\) \(\mu_0\) for decreasing magnitudes of the magnetic field, yet the magnetization rapidly vanishes at the lowest fields showing a marginal or zero remanent magnetization. On the other hand, at 4.2 K, we find an open hysteresis loop with a remanent magnetization of 0.07–0.08 \(N_a\) \(\mu_0\), a coercivity of 0.07–0.08 T, and magnetization steps at ca. \(\pm 0.02\) T (and maybe another pair of steps at ca. \(\pm 0.06\) T).

Since the magnetization does not reach saturation at 5.0 T, and since the \(M_m\) value of 1.7 \(N_a\) \(\mu_0\) is well below the estimated saturation value of 4.6 \(N_a\) \(\mu_0\) (i.e. 2.3 \(N_a\) \(\mu_0\) per Ni\(^{II}\) center, derived from \(M_m,\text{sat} = g_\text{eff} S_\text{eff} N_a\mu_0\)), the ground state of 1 cannot be characterized by fully collinear ferromagnetic exchange interactions. Thus, either a minor amount of exchange pathways with antiferromagnetic interactions is present within the compound, or chains or areas of opposing magnetic moments exist in the rather complicated structure (or some combination of both). Considering that magnetization values for paramagnetic compounds decrease with increasing temperatures at a constant applied field, \(M_m\) at 5.0 T should be larger at 2.5 K than at 4.2 K. This is not observed. In addition, since the behavior of the magnetization drastically changes, the magnetization rather indicates a structural phase transition between 2.5 K and 4.2 K. Besides the observation of hysteresis at 4.2 K, the magnetization steps point to the presence of a (thermally assisted) resonant tunneling mechanism as known for example, for quasi-zero dimensional spin systems such as SMMs. One prerequisite for the presence of such a mechanism is a magnetically anisotropic system, which can be assumed for 1 given its structure. However, 1 represents an extended infinite spin system; a porous metal organic framework composed of chains and knots of Ni\(^{II}\) centers, at the same time, the complex magnetic exchange topology of 1 does also not constitute a classical three-dimensional bulk ferromagnet.

To gain further insight into the magnetism of 1, we also probed dynamic magnetic fields of various frequencies in the absence of a static bias field. The corresponding ac susceptibility data are shown in Figure 4–Figure 6. As evident from the temperature dependence of the out-of-phase molar magnetic susceptibility \(x_m''\) (Figure 4), there are two temperature ranges in which \(x_m''\) significantly differs from zero: between 17 and 25 K and between 2.0 and 3.0 K. In the higher temperature range, shown in detail in the insets of Figure 4, the out-of-phase signal is small, but shows a temperature dependence that is similar to a phase transition to long range ordering in a 3D ferromagnet, yet the order of magnitude is much smaller for 1. On the other hand, compounds composed of a few interacting paramagnetic centers—except for SMMs—do not show such a characteristic feature. According to structural information, 1 is a three dimensional, rather asymmetrical mesh with large vacancies that could allow for a partial ordering along for example, the Ni\(^{II}\) chains and/or knots, analogous to the long-range ordering in a ferromagnet. From the inflection point of \(x_m''\) vs. \(T\), the corresponding ordering temperature amounts to \(T_c = (23.9 \pm 0.2)\) K.

Relevant out-of-phase signals at the lowest temperatures span a very small range of less than 1 K between 2.0 and 3.0 K; the signals vanish below 2.0 K and above 2.8 K. The maximum values of \(x_m''\) are much larger compared to the ones observed...
at 17 to 25 K. Since the $\chi''$ vs. $f$ curves at 2.4 K and 2.5 K reveal maxima (Figure 5), as also evident from the Cole–Cole plot ($\chi''$ vs. $\chi'$, Figure 6), we analyzed the data in terms of a generalized Debye expression. However, none of the fits could reasonably reproduce the data. Introducing several types of restrictions also failed to model the data using the extended Debye expression, which leads to the conclusion that the ratio of the (average) conserved energy to the dissipated energy per cycle depends on the applied frequency of the magnetic field.

Thus, relaxation processes solely caused by magnetic ordering are highly unlikely. Considering the very steep and narrow maxima observed in the $\chi''$ vs. $T$ and $\chi''$ vs. $T$ curves that occur within a very small temperature interval (ca. 2.1–2.6 K, Figure 4), the relaxation processes are potentially rather fast compared to the characteristic timescales of SMMs.

Combining the analyses of ac and dc magnetic data of 1, leads us to conclude a partial magnetic ordering for $T < 23.9$ K, and another magnetic ordering process at about 2.8 K, which presumably additionally involves a structural phase transition. The identified magnetic properties can be qualitatively rationalized from the structural properties of 1. The chains and the Ni$_4$O$_4$ cubanes consist of close neighboring Ni$^{II}$ centers with Ni–Ni distances less than 3.1 Å and Ni-O-Ni angles ranging from 90.8° to 99.8°, that is, between 90° and 100°. While the distance is correlated to the magnitude of the exchange interactions (the closer, the larger), the angles determine the type of interaction considering the well-known Kramers–Anderson superexchange model. For most Ni-O-Ni angles, the exchange interaction are antiferromagnetic, in particular, for most obtuse angles larger than about 100°. However, for Ni-O-Ni angles close to 90°, the interaction becomes ferromagnetic. Therefore, the Ni$^{II}$ centers forming the chains as well as the cubanes are likely the origin of the predominantly ferromagnetic
interactions of 1. The chains and the cubanes are linked by OH· groups yielding closest Ni···Ni distance of 3.4 Å and Ni-O-Ni angles of 118°. Thus, the interactions via these exchange pathways are likely to be antiferromagnetic and weaker than the ferromagnetic interactions within the chains and cubanes, providing an explanation for the observed magnetization data.

Conclusions

In conclusion, a 3D MOF based on perpendicular 1D Ni²⁺ linear chains interconnected via Ni₃O₆ cubanes has been synthesized, offering a rare example of a magnetic material that shows several partial magnetic ordering phenomena: one at \( T < 23.9 \) K, and another process at about 2.8 K, likely associated with a structural phase transition. These results demonstrate the concept of utilizing MOF architectures to connect extended spin structures with molecular spin clusters in order to realize novel or complex magnetic-ordering phenomena.

Experimental Section

Elemental analyses were performed on a Carlo Erba EA 1108

FTIR spectra (KBr pellets, 400–4000 cm⁻¹) were recorded on a Thermo Nicolet Avatar 320 spectrometer. Magnetic data of 1 were recorded using a Quantum Design MPMS-SXL SQUID magnetometer. The polycrystalline sample was compacted and immobilized into a cylindrical PTFE capsule. DC susceptibility data were acquired as a function of the magnetic field (−5.0 to +5.0 T at 4.2 K) and temperature (2.0–300 K); ac data were measured in the absence of a static bias field in the frequency range 1–1000 Hz (\( T = 1.9–50 \) K, \( B_{ac} = 3 \) G). Data were corrected for the diamagnetic contributions of the sample holder and the compound (\( \chi_{dia} = −1.78 \times 10^{-4} \text{cm}^3\text{mol}^{-1}\)).

Powder X-ray diffraction data were recorded on a Philips X’Pert diffractometer (CuKα, \( \lambda = 1.54056 \) Å) to check the purity of bulk samples of 1 (Figure S1 in the Supporting Information). Thermogravimetric analyses were performed under nitrogen flux using a Mettler Toledo TGA/SDTA 851 at a heating rate of 10 °C min⁻¹ to assess the thermal stability of 1 (Figure S2 in the Supporting Information). 1 is thermally stable up to 380 °C. An initial weight loss (ca. 5%) starting at 150 °C is due to loss of one water molecule coordinated to Ni₃ (calc. 5.06%) in the framework. At higher temperatures the weight remains constant, followed by sudden decrease in the weight, suggesting the onset of decomposition around 380 °C with a total weight loss of 55.3% (calc. 57.98%), resulting in simple oxides (NiO). Suitable single crystals of 1 (0.13 × 0.10 × 0.05 mm³) were used in the intensity data collection using a Bruker SMARTAPEX CCD diffractometer at 150(2) K (\( \lambda = 0.71073 \) Å). The structures were solved by direct methods and refined by full-matrix least squares against \( F^2 \) using the SHELSX-97 and SHELXL-97 programs.[13] Anisotropic thermal parameters were assigned to all non-hydrogen atoms. The hydrogen atoms were set in calculated positions and refined as riding atoms with a common fixed isotropic thermal parameter. Analytical expressions of neutral atom scattering factors were employed, and anomalous dispersion corrections were incorporated.

Synthesis of 1

A mixture of 0.5 mmol of 1,4-phenylene diacetic acid (0.097 g) and 2 mmol of KOH (0.112 g) in 6 mL distilled water was stirred for 10 minutes followed by addition of a solution of NiCl₂·6H₂O (1 mmol, 0.237 g) in 4 mL H₂O. The resulting solution was sealed in a 23 mL Teflon-lined stainless steel autoclave and heated to 170 °C for three days under autogenous pressure. The reaction vessel was then cooled to room temperature over 4 hours. Green diamond-shaped crystals of 1 suitable for single-crystal X-ray diffraction analysis were collected from the final reaction system by filtration and dried in air at ambient temperature (42% yield based on Ni). Anal. calc: C, 33.7% H, 1.7%. Found: C, 33.4% H, 3.31%. IR data (\( \nu_{\text{vibr}} \) cm⁻¹): 3672 s, 3591 s, 3569 s, 3535 s, 2965 w, 2930 m, 1607 s, 1556 w, 1427 s, 1386 s, 1280 m, 1202w, 1138 m, 940 s, 803 s, 737 s (Figure S3).

Crystallographic data for 1

\( \text{C}_{38}\text{H}_{30}\text{Ni}_{16} \text{O}_{22} \), \( M_r = 355.57 \text{g mol}^{-1} \), tetragonal, space group \( \text{I}4/\text{a} \), \( a = 12.1839 (6), b = 12.1839 (6), c = 33.0206 (18) \) Å, \( V = 4901.8 (4) \) Å³, \( T = 150(2) \) K, \( Z = 16 \). \( R_{\text{wp}} = 0.1927 \text{g cm}^{-3} \), \( \lambda = 0.71074 \) Å, 8548 reflections collected, 1812 unique (\( R_{\text{wp}} = 0.037 \)), \( R(F^2 > 2\sigma(F)) = 0.031 \) and \( wR(F^2) = 0.086, S = 1.06 \).

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Conflict of interest

The authors declare no conflict of interest.

Keywords: cubanes · magnetic materials · metal-organic frameworks · nickel · phase transitions

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