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Novel 3-D Framework Nickel(II) Complex with Azide, Nicotinic Acid, and Nicotinate(1–) as Coligands: Hydrothermal Synthesis, Structure, and Magnetic Properties

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The hydrothermal reaction of $Ni(NO_3)_2$, NaN_3, and nicotinic acid (Hnic) yielded a 3-D supramolecular framework complex, $[Ni_{1.5}(N_3)(nic)_2(Hnic)]_n$ (**1**) with unusual magnetic properties. In **1**, Hnic and nic^{-1} coexist and show different coordination modes (μ_2-Hnic-*N*,*O*, μ_2-nic-*N*,*O*, and μ_3-nic-*N*,*O*,*O* bridging Ni^{II} ions), and azide groups adopt μ-1,1 (EO) bridging mode linking Ni^{II} ions with an unusual Ni–N–Ni angle.

The investigation of molecule-based magnetic materials with novel structure has become a fascinating subject in the fields of material chemistry and inorganic chemistry.[1] As a versatile bridging ligand with various exchange pathways, the azide ligand is a good candidate for the design of magnetic coordination polymers.[2] In this sense, several 1-, 2-, and 3-D complexes have been reported.[3−5] However, because of the possibility of explosion, azide must be handled carefully; thus, as an efficient synthesis method, hydrothermal reaction has seldom been applied in the synthesis of such complexes. An interesting strategy toward high-dimensional framework derivatives is to incorporate a second bridging ligand into the metal−azido systems.[6] As for the compounds reported to date, most of the coligands are neutral organic ligands, while charged ligands are very scarce.[7] Synthesizing high-dimensional compounds with azide and negative ligands represents a challenge for researchers of this topic. Commonly, it is difficult for two different kinds of negative ligands to coexist in the same molecule because of their competition in the process of self-assembly. Fortunately, we successfully isolated a 3-D azide Ni^{II} compound, $[Ni_{1.5}(N_3)(nic)_2(Hnic)]_n$ (**1**) with nic (and Hnic) as coligands, by the hydrothermal reaction method.[8] X-ray analysis[9] revealed that the asymmetric unit of **1** contains one and a half Ni atoms, one azide ligand, one Hnic molecule, and two nic anions (Figure S1 of the Supporting Information), in which each Ni^{II} ion is coordinated in a distorted octahedral geometry. The Ni1 ion, being located at a crystallographic inversion center, is coordinated by two N atoms [Ni1−N4 = 2.127(3) Å] from two azide groups, two N atoms [Ni1−N3 = 2.097(3) Å] from two Hnic groups, and two carboxylate oxygen

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(8) Compound **1** was hydrothermally synthesized under autogenous pressure. A mixture of $Ni(NO_3)_2 \cdot 6H_2O$, NaN_3, Hnic, and H_2O at a ratio of 2:1:2:500 was sealed in a Teflon-lined autoclave, heated to 160 °C for 2 days, and cooled to room temperature at 10 °C h^{-1}. The crystals were obtained in ca. 30% yield based on nickel. Selected IR (KBr, cm^{-1}): 2060, 1674, 1614 and 1391. Anal. Calcd for $C_{36}H_{26}Ni_3N_{12}O_{12}$ (993.81): C, 43.5; H, 2.6; N, 16.9. Found: C, 43.8; H, 2.2; N, 17.3. Attempts for synthesizing **1** using the methods in ref 7b were not successful. **Caution!** Azide complexes are potentially explosive. Only a small amount of the materials should be prepared and handled with care.

(9) Crystal data for **1**: triclinic, $P\bar{1}$, $a = 8.6311(11)$ Å, $b = 11.3015(14)$ Å, $c = 11.9468(15)$ Å, $\alpha = 112.066(2)°$, $\beta = 100.134(2)°$, $\gamma = 108.468(2)°$, $V = 965.0(2)$ Å^3, $Z = 1$, λ(Mo Kα) = 0.710 73 Å, 5279 reflections collected, 3532 unique ($R_{int} = 0.0257$), R1 = 0.0358, wR2 = 0.1024 [$I > 2\sigma(I)$]. CCDC No. 268808.

10.1021/ic051030b CCC: $30.25

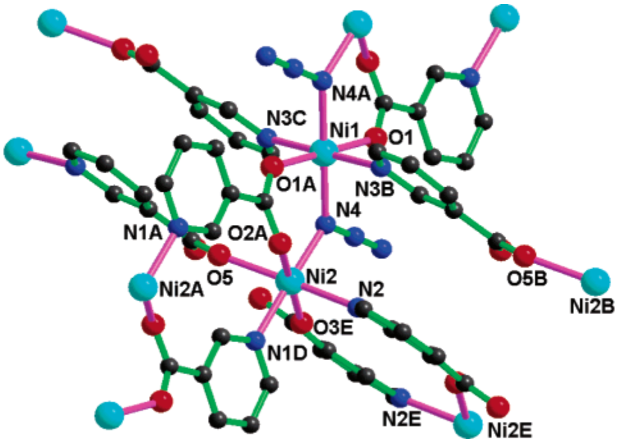

Figure 1. Coordination and linkage modes of ligands and Ni^{II} ions in **1**.

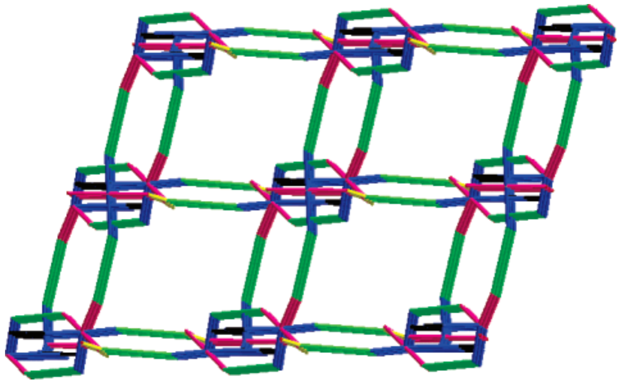

Figure 2. 3-D structure of **1** with organic ligands simplified.

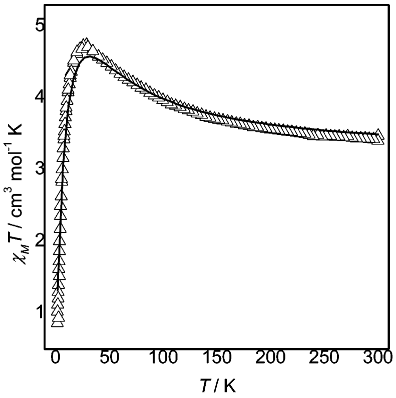

Figure 3. Plot of $\chi_M T$ vs T for **1**. The solid line represents the best fit of applying the formula for a trinuclear Ni^{II} complex by the mean-field approach.

atoms [Ni1−O1 = 2.077(2) Å]. The Ni2 atom is coordinated by an azide N atom [Ni2−N4 = 2.092(3) Å], two N atoms [Ni2−N2 = 2.139(3) Å; Ni2−N1A = 2.108(3) Å] from two nic ligands, and three oxygen atoms [Ni2−O2a = 2.066(2) Å; Ni2−O3a = 2.074(2) Å; Ni2−O5 = 2.091(2) Å] from three nic ligands. As shown in Figure 1, the azide ligands take EO bridging mode, while the nic ligands act in two modes (Scheme S1 of the Supporting Information): one is tridentate μ_3-*N*,*O*,*O* (syn−syn), and the other is bidentate μ_2-*N*,*O*. Such a coordination mode is different from that in the analogue Mn^{II} complex,[7b] in which the nic coligand acts as a tridentate μ_3-*N*,*O*,*O* mode only. Azide, together with a tridentate nic, links Ni^{II} ions to form a 1-D chain, which is linked to adjacent chains by bidentate nic groups to form a 2-D sheet (Figure S2 of the Supporting Information). Further, the Hnic ligands also adopt a bidentate mode to link the 2-D sheets into a 3-D network (Figure 2).

The basic building block of complex **1** is the trinuclear Ni3 entity, which contains two bridging N_3 ligands, EO, and syn−syn carboxylate. The former most often shows ferromagnetic coupling,[10] while the later displays antiferromagnetic coupling.[9] In the first case, the Ni−N−Ni angle is very important for the magnitude of the ferromagnetic coupling.[11] This angle, for **1**, is 125.22°, greater than those reported for the typical double EO dinuclear complexes (∼104°). This difference, together with the simultaneous presence of the syn−syn carboxylic bridge, should give a decrease in the ferromagnetic J value (the average value for double end-on azido complexes is ca. 40 cm^{-1}).[10] The bridges that link these trinuclear entities to form the 3-D net are pyridine−carboxylic ligands, giving long distances between adjacent Ni^{II} ions. This J' coupling must be, thus, small compared to that created within the trimeric entity.

The magnetic properties of complex **1** as a $\chi_M T$ vs T plot (χ_M is the molar magnetic susceptibility for three Ni^{II} ions, measured at 0.1 T) are shown in Figure 3. The value of $\chi_M T$ at 300 K is 3.5 cm^3 K mol^{-1}, which is as expected for three magnetically quasi-isolated $S = 1$ ions ($g > 2.00$). Starting from room temperature, $\chi_M T$ values increase to 45 K, with a maximum $\chi_M T$ value of 4.8 cm^3 K mol^{-1}. Below 45 K, there is a clear decrease to approximately 1 cm^3 K mol^{-1} at 2 K. This feature is characteristic of noticeable ferromagnetic interactions within the trinuclear entities and antiferromagnetic interactions between them. Furthermore, the presence of the D parameter for the Ni^{II} ions may also be the reason for the clear decrease in the low-temperature region. The reduced molar magnetization at 2 K (Figure S3 of the Supporting Information) clearly corroborates this global antiferromagnetic behavior at low temperature (or, once again, the presence of an important zero-field-splitting parameter). The $M/N\beta$ curve does not follow the Brillouin shape, and at 5 T, the $M/N\beta$ value is close to 4.6 $N\beta$ instead of 6 (the value for three Ni^{II} ions ferromagnetically coupled, assuming $g = 2.00$).

The magnetic pathways in complex **1** are shown in Scheme 1. To fit the experimental values, we have made several approaches. The first one was to consider only the high-temperature region, cutting the experimental curve at different temperatures and fitting with the typical formula given in the literature for a linear trinuclear Ni^{II} complex, using the Hamiltonian $H = -J\sum S_iS_j$.[12] As can be seen from Figure S4 of the Supporting Information, the best fit is obtained by cutting at 100 K with the following parameters: $J = 21.7$ cm^{-1}, $g = 2.05$, and $R = 1.9 \times 10^{-4}$. Considering thus that

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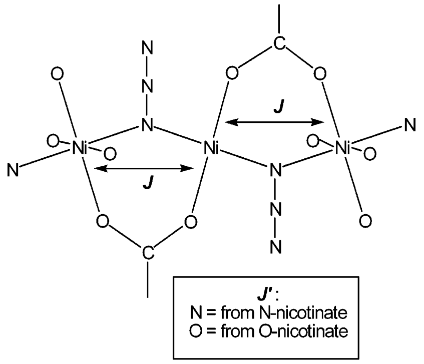
Scheme 1. Magnetic Pathways for **1**



the *J* value is close to 21−22 cm^{-1}, we treat to fit all experimental values assuming either *J*′ (intramolecular coupling parameter, evident in this 3-D net) or the existence of a *D* parameter, which cannot be omitted in Ni^{II} complexes, being on the order of 4−7 cm^{-1}. Unfortunately, both parameters, *J*′ and *D*, have the same effect and cannot be studied simultaneously because they are strongly correlated.

Thus, in a first approach, we fit the experimental data with the same formula as that for a trinuclear Ni^{II} complex but introducing in the fit a *J*′ value, by means of the mean-field approximation.[13] The results are shown in Figure 3, giving the following best parameters: $J = 24.5$ cm^{-1}, $J' = -1.32$ cm^{-1}, $g = 2.07$, and $R = 3.3 \times 10^{-3}$. Finally, we tried to simulate the experimental curves using the MAGPACK program,[14] fixing $J = 22$ cm^{-1} and $g = 2.06$ and varying *D* from 6 cm^{-1} (a very realistic value) to 25 cm^{-1} (an unrealistic value for Ni^{II} ions). Figure 4 clearly shows that, even when *D* is 25 cm^{-1}, the theoretical curve, at low temperatures, is very far from the experimental one. However, the simulation is very good at higher temperatures. As a conclusion, we deduce that the two factors (*J*′ and *D*) are important and cannot be neglected but the intertrimer interaction (*J*′) is more important than the *D* parameter. With *J*′, we found a good fit, whereas with only *D*, it was impossible to have a good fit of the experimental data.

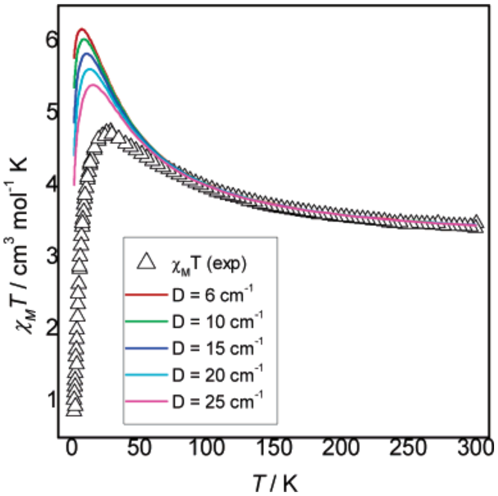


Figure 4. Plot of $\chi_M T$ vs *T* for **1** compared to the curves obtained with different *D* values.

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Supporting Information Available: The views of the molecule and 2-D network of **1**, the coordination modes of Hnic and nic in **1**, the related magnetic plots of **1**, and the crystallographic data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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