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Novel Heterometallic 3d–4f Metal–Azido Complex of Mixed Ligands with Unprecedented Structure Type: Synthesis, Structure, and Magnetic Properties

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A novel heterometallic 3d–4f metal–azido complex of mixed ligands, showing unprecedented structure type and interesting magnetic properties, has been hydrothermally synthesized and characterized.

The synthesis of heterometallic (3d−3d and 3d−4f) complexes is of current focus, which is justified not only by the fascinating structural diversity of such complexes but also by their potential applications as functional materials in magnetism, molecular adsorption, light conversion devices, and bimetallic catalysis.[1] Metal−azido complexes have attracted great attention because azide is an excellent candidate for the design of magnetic materials.[2] From the structural perspective, the diverse bridging modes of azide can provide a series of novel structures in which it acts as an efficient magnetic coupler.[3] From the magnetic point of view, the coordination modes of the azide ligands associated with structural parameters (bond angles and lengths, etc.) greatly affect the nature and magnitude of the magnetic exchange interactions in these systems.[4] The metal−azido derivatives of high-dimensional networks are of particular interest.[5] Commonly, there are two main strategies that have been employed in this field: one is to increase the number of azide ligands by adding a countercation, and another is the introduction of a second bridging ligand to extend the architectures.[6] With this perspective, what is going to occur with the lanthanide as the countercation and isonicotinic acid as the second bridging ligand? We decided to make the reaction by a hydrothermal method. Fortunately, we succeeded in synthesizing and fully characterizing a new unique compound: $[GdNi_2(isonic)_5(N_3)_2(H_2O)_3]\cdot 2H_2O$ (**1**).[7] To our knowledge, this is the first example of 3d and 4f metal ions coexisting in the metal−azido derivatives.

The structure[8] of complex **1** displays a complicated three-dimensional structure, containing one Gd^{III} ion, two unique Ni^{II} (Ni1 and Ni2) ions, two unique azide ligands, and five

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(7) Synthesis of complex **1**: Complex **1** was hydrothermally synthesized under autogenous pressure. A mixture of $Gd(NO_3)_3\cdot 6H_2O$, $Ni(NO_3)_2\cdot 6H_2O$, NaN_3, isonicotinic acid, and H_2O in the ratio of 1:2:2:5:2000 was sealed in a Teflon-lined autoclave and heated to 140 °C for 2 days. The crystals were obtained in ca. 30% yield based on Ni. Elemental analysis is satisfactory. ***Caution!*** *Azide complexes are potentially explosive. Only a small amount of the materials should be prepared and handled with care.*

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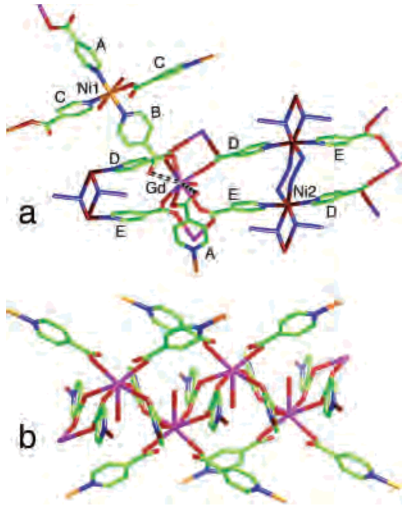

Figure 1. (a) Local coordination geometry around the metal ions in **1**. Color scheme: Gd, purple; Ni1, orange; Ni2, brown; C, green; O, red; N, blue. H atoms are omitted for clarity. The striped bonds represent the longer Gd−O interactions, and the five unique isonicotinate ligands are denoted as A−E. (b) Connection of Gd^{III} by the tridentate isonicotinate into one-dimensional chains (longer Gd−O interactions are not shown).

different isonicotinate anions, two of which are tridentate and three of which are bidentate. The structure also contains water molecules coordinated to the Gd^{III} ions (one each), and to the Ni1 ions (two each, in a trans arrangement), and also uncoordinated water molecules trapped within the lattice. The local connectivity and coordination geometries are shown in Figure 1a. Selected bond lengths and angles are given in Table S1 of the Supporting Information.

The Gd^{III} ions are seven-coordinate, although there are two interactions to carboxylate O atoms (belonging to carboxylates with the other O already bound to the metal), which are not substantially longer than the other seven Gd−O bonds; these are shown as striped bonds in Figure 1a. Each Gd^{III} ion is bound to four tridentate isonicotinates, two bidentate isonicotinates, and a water molecule. The tridentate isonicotinate anions bridge the Gd^{III} ions into one-dimensional zigzag chains via the carboxylate groups (Figure 1b). These tridentate isonicotinate anions also coordinate to Ni2 ions via the N atoms. The Ni2 ions are, in turn, connected into chains by two alternating types of double azide bridges. One type contains two anions bridging in the end-on (EO) mode, and the other type contains two end-to-end (EE) anions. This results in two-dimensional sheets of alternating Gd/RCO_2 and $Ni2/N_3$ chains linked by the isonicotinate N−Ni2 bond (Figure 2a). Meanwhile, the three different bidentate isonicotinate ions coordinate to the Ni1 ions (Figure 1a) in an equatorial arrangement. One type of bidentate isonicotinate bridges the Ni1 ions into linear chains, coordinating via its pyridyl N to one Ni1 and via a carboxylate O to another. Thus, each Ni1 coordinates to one of these ligands via the N, and to another, trans from the first, via an O atom. The other two equatorial positions are occupied by the remaining two types of bidentate isonicotinate anions. These anions are N-bound and connect the Ni1 cations to the Gd^{III} ions: one to a Gd/Ni2 sheet below and one to a Gd/Ni2 sheet above. Thus, the Gd/Ni2 sheets are connected via the Ni1 ions into a single three-dimensional network. In the complicated overall topology (Figure 2b), the Gd^{III} ions act as six-connecting nodes, the Ni1 and Ni2 ions act as approximately planar four-connecting nodes, and the tridentate isonicotinate anions act as three-connecting nodes.

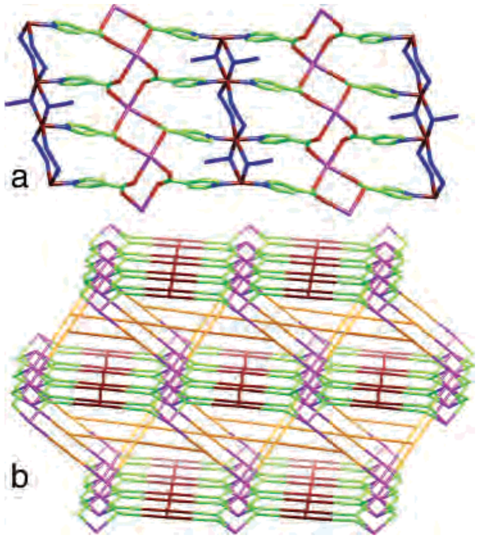

Figure 2. (a) Two-dimensional sheet of Gd/RCO_2 and $Ni2/N_3$ chains cross-linked by the isonicotinate N−Ni bonds. (b) Schematic view of the overall three-dimensional net connectivity, viewed slightly offset from the *a* axis. All connections by the bidentate isonicotinates or double azide bridges are replaced by direct connections between the metal atoms involved (metal nodes colored as before), while the tridentate isonicotinate anions are represented by just their carboxylate C (green nodes).

From magnetic point of view, it is convenient to analyze separately the possible behaviors of each nonequivalent cation (Gd^{III}, Ni1, and Ni2) in **1**: (a) Gd^{III} ions form a pseudo-one-dimensional net in which each one is linked to two neighbors through two carboxylates in syn−anti coordination mode, (b) Ni2 ions form an one-dimensional alternating EO and EE azide system, and (c) Ni1 ions are simply linked by pyridinecarboxylate bridges. Thus, an accurate fit of the magnetic data in this system is beyond any possibility. However, if we take into account several features, we can conclude that the only important part in the whole structure is the alternating EO−EE N1−azido system. Indeed, the coupling between Gd^{III} ions is always very small,[9] and the syn−anti carboxylate pathway always gives small magnetic coupling even for Cu^{II} ions. The Ni1 ions linked by pyridinecarboxylate bridges can only give a very small coupling. Figure 3a clearly corroborates this hypothesis: the reduced magnetization at 2 K tends to $9N\beta$. Considering the unit $GdNi_2$, we have 11 electrons at the limit of saturation. However, as is well-known in the literature, the alternating EO−EE Ni coordination mode corresponds to an alternating ferromagnetic−antiferromagnetic chain,

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(8) Crystal data for complex **1**: monoclinic, $P2(1)/n$, $a = 8.1859(9)$ Å, $b = 26.853(3)$ Å, $c = 16.8859(18)$ Å, $\beta = 95.351(2)°$, $V = 3695.6(7)$ Å^3, $Z = 4$, λ(Mo Kα) = 0.710 73 Å, 23 167 reflections collected, 8701 unique ($R_{int} = 0.0465$), R1 = 0.0283, wR2 = 0.0789 [$I > 2\sigma(I)$], CCDC no. 281775.

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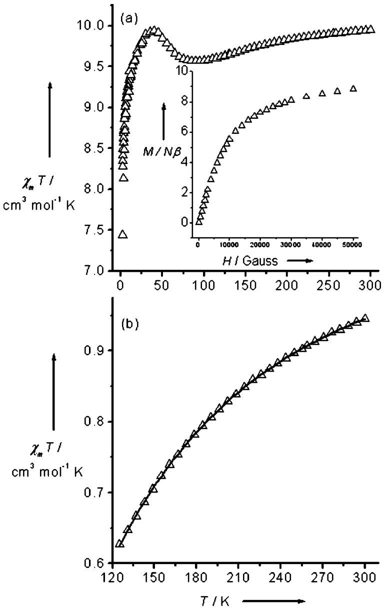

Figure 3. (a) Plot of $\chi_m T$ vs T for **1**. Inset: plot of the reduced magnetization at 2 K for **1**. (b) Plot of $\chi_m T$ vs T for **1** in the interval 125−300 K (open triangles). The solid line represents the best fit obtained with the parameters indicated in the text.

generally with noticeable J values. If we subtract from the theoretical value of 11 electrons the 2 electrons corresponding to this chain, we obtain, precisely, the value of $9N\beta$, as experimentally occurs. In this treatment, logically, we do not take into consideration the g value of the Ni^{II} ions, which is >2.00.

This feature corroborates that the interaction among Gd^{III} ions themselves is very small[9] and the interaction among Gd^{III} and Ni^{II} through pyridinecarboxylate will be small, which corresponds to the long distance and lack of any important magnetic pathway through this carboxylate. Furthermore, assuming any small magnetic coupling, it will likely be ferromagnetic because the coupling between Ni^{II} and Gd^{III} is experimentally ferromagnetic.[10] Finally, the coupling between Ni^{II} ions through the same carboxylate ligand will be very small, almost negligible. If any, it will likely be antiferromagnetic.

The plot of $\chi_m T$ vs T values is shown in Figure 3a. From 300 to 100 K, there is a decrease from ca. 10 to 9.6 cm^3 mol^{-1} K. When the temperature is decreased, there is a clear increase to 10 cm^3 mol^{-1} K and from 50 K a pronounced decrease to 7.5 cm^3 mol^{-1} K at 2 K. Thus, we can divide the curve into two parts: the first one (from room temperature to ca. 40 K) results from the contribution of the ferrimagnetic coupling (Ni−Gd) and the contribution of the coupling in the Ni−Ni azide chain (F and AF). The second one (from 40 to 2 K) is the clear decrease of $\chi_m T$ likely due to the zero-field splitting of Ni^{II} ions.

At low temperatures, all components of the whole net can be important, but as indicated above, at high temperature, only the azido−Ni chain seems to be magnetically important. Thus, cutting the $\chi_m T$ curve at 125 K and subtracting the theoretical $\chi_m T$ values due to one Gd^{III} and one Ni^{II} (not coupled; ca. $7.87 + 1.1 = 9$ cm^3 mol^{-1} K), we have fit the values using the El Fallah formula for these kinds of $S = 1$ alternating systems, which is completely valid at these temperatures.[11] The El Fallah formula is double: assuming the alternation parameter between 0 and 2 or between 2 and 6. Using the two different formulas, the best fit was found with the first ($0 < \alpha < 2$) with the following values: $J_{AF} = -65.3 \pm 0.3$ cm^{-1}, $\alpha = 0.39 \pm 0.03$ (which represents $J_F = 26.1$ cm^{-1}), $g_{average} = 2.13$, and R (agreement factor) $= 4.6 \times 10^{-6}$ (Figure 3b).

It is important to underline that, with all of these simplifications, these J values perfectly agree to those reported in the literature for these kinds of systems. For example, the EE part depends on the δ angle (between the plane formed by the two azido bridges and the N−Ni−N plane). In **1**, this plane is 22.8°. According to the literature,[12] when this plane is close to 0°, the J value can be less negative than -100 cm^{-1}. For δ angles close to 20°, the J values are less AF, varying from -40 to -80 cm^{-1}, depending on the other factors (distances, other distortions, etc.).[12] Thus, the J value calculated for **1**, -65.3 cm^{-1}, is in perfect agreement with that expected.

For EO systems, according to the literature,[12] the J values depend mainly on the Ni−N−Ni angle. This angle is always very close to 100°, as in **1**. All of the J values reported in the literature are between 25 and 70 cm^{-1}, being dependent on the torsion angle between the N_3 bridge and the Ni−N−Ni−N rhombus. This torsion tends to diminish the ferromagnetism. In **1**, this angle is 33°. The experimental J value of $+26.1$ cm^{-1} seems, thus, consistent for this kind of structure.

In conclusion, we have successfully obtained a three-dimensional heterometallic 3d−4f metal−azido complex of mixed ligands by hydrothermal synthesis, which is the first report of such complexes in this field. The synthesizing method has been proven to be an effective way to obtain such complexes. The magnetic properties have been studied, and we expect that those complexes will find applications such as in magnetic materials.

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Supporting Information Available: X-ray crystallographic data in CIF format and selected bond lengths and angles for **1** (Table S1). This material is available free of charge via the Internet at http://pubs.acs.org.

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