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First Metal Azide Complex with Isonicotinate as a Bridging Ligand Showing New Net Topology: Hydrothermal Synthesis, Structure, and Magnetic Properties

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A new 3D azido-bridged coordination polymer, $[Co_{1.5}(N_3)(OH)(Isonic)]_n$ (**1**), has been synthesized and characterized and its magnetic properties studied. Isonicotinate acts as a bridging coligand in this complex. In **1**, all of the ligands take tridentate bridging coordination modes, and the overall structure of **1** exhibits a new 3,6-connected net topology.

The design and magnetism of coordination polymers are of considerable current interest not only for understanding the fundamental science of magnetic interactions but also for developing new materials.[1] The key for designing such materials is to search for good bridging ligands that can effectively mediate the magnetic coupling.[2] Azide is a suitable candidate because of its diversity in the structure and magnetism of its complexes.[3] In most cases, bridging azide ligands take end-to-end (EE) and end-on (EO) coordination modes. In general, the EE mode affords antiferromagnetic exchange, while the EO mode shows ferromagnetic exchange interactions, and other mixed azide bridging modes also give interesting magnetic properties.[4] In the past 2 decades, several mono- and multidimensional metal−azido derivatives were reported.[5]

Because it is believed that through increasing the lattice dimensionality it is possible to enhance the bulk magnetic properties,[6] high-dimensional metal−azido complexes are the targets for researchers. Therefore, one of the most effective strategies is the introduction of a second ligand to extend the architecture.[7] The reasonable selection of the coligand is a challenge: pyridine, Schiff base, and polyamine derivatives, which are all neutral, were well used as coligands,[8] while negative coligands are scarcely studied[9] because it is difficult to synthesize the coligating complexes because of the presence of two different kinds of negative ligands that must coexist and compete in the same molecule. Isonicotinate is a negative ligand and has not been well applied in the metal−azido complexes. In the past, isonicotinate, which successfully coordinated to metal−azido complexes, in effect was an ester and acts as a neutral ligand.[10] In this work, we successfully isolated, by hydrothermal reaction, a 3D azide−Co^{II} complex, $[Co_{1.5}(N_3)(OH)(Isonic)]_n$ (**1**) with isonicotinate as the coligand.[11] It is the first metal azide complex in which isonicotinate acts as a bridging ligand. Furthermore, the overall structure of **1** shows a new 3,6-connected net topology.

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X-ray analysis[12] revealed that the asymmetric unit of **1** contains one and a half Co atoms, one isonicotinate anion, an azide anion, and a hydroxide anion that was calculated by the valence sum calculations[13] with the value of 1.069 (Figure S1 in the Supporting Information). Co1 coordinates to two cis azide anions, two cis hydroxide anions, one oxygen, and one nitrogen of two separate isonicotinate anions, in a trans arrangement. Co2 lies on an inversion center (all other atoms lie at general positions) and coordinates to two trans azide anions, two trans hydroxides, and oxygens of two trans isonicotinate anions. All of the coordination bonds lie within normal distances (Table S1 in the Supporting Information). In **1**, the azide, the isonicotinate, and even the OH all perform tridentate bridging coordination modes, so all ligands each bridge one Co2 and two Co1 ions.

The complicated 3D network created can be described in terms of sheets of $[Co_3(OH)_2(N_3)_2]^{2+}$ pillared by isonicotinate anions (Figure 1a). The sheets contain $[Co_3(OH)_2(N_3)_2]^{2+}$ subunits, one of which is highlighted in the figure. Two Co1 ions are connected to a Co2 ion, each by a hydroxide, an azide (EE), and a carboxylate bridge belonging to the isonicotinate pillar. Each subunit is then connected directly to four adjoining subunits via both azide and hydroxide bridges, to give a polymeric 2D motif. Alternatively, the sheet could also be described in terms of chains of Co1 ions bridged by hydroxide and azide anions (the chains run in a horizontal direction in Figure 1a). These chains are then cross-linked to give the sheet via Co2 ions, which are connected via the azide, hydroxide, and carboxylate bridges.

These layers are then cross-linked by the isonicotinate bridges to give an overall complicated 3D network (Figure 1b). If the metals are considered to be 6-connecting nodes and the ligands 3-connecting nodes, then a 3,6-connected net is formed, which contains two types of 6-connecting nodes and three types of 3-connecting nodes (Figure S2 in the Supporting Information). Nets containing only nodes with connectivity shown by commonly used metal ions and ligands (i.e., 3-, 4-, and 6-connecting nodes) are particularly important in coordination polymer analysis; this net represents a new 3,6-connected net topology.[14]

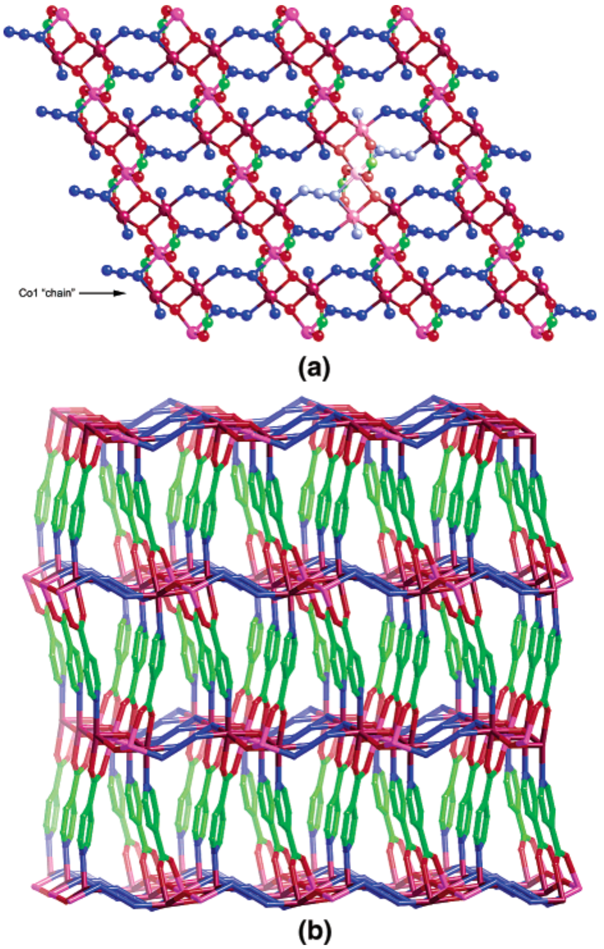

Figure 1. (a) View of the sheet substructure motif in **1**. A $[Co_3(OH)_2(N_3)_2]^{2+}$ subunit is highlighted by pale-colored atoms, while the direction of the Co1 "chains" is also indicated (see the text). For clarity, only the carboxylate and nitrogen of the interlayer Isonic bridges are shown. Color scheme: Co1, red-brown; Co2, purple; N, blue; C, green; O, red. (b) View of the 3D network generated by the bridging of layers by Isonic anions.

From a magnetic point of view, in almost all octahedral Co^{II} complexes, the $\chi_M T$ (or μ_{eff}) values at room temperature are greater than those expected for an isolated spin-only ion ($\chi_M T = 1.87$ cm^3 mol^{-1} K for a $S = {}^3/_2$ ion), indicating that an important orbital contribution is involved.[15] Typical values of $\chi_M T$ (or μ_{eff}) are 2.75−3.4 cm^3 mol^{-1} K (4.7−5.2 μ_B). Lower values at room temperature indicate perturbation from ideal octahedral geometry.[15] Considering the spin−orbit coupling due to the $^4T_{1g}$ ground state for octahedral Co^{II} complexes together with their distortion, exact calculations for deriving the J parameter from experimental data in the

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(11) Complex **1** was synthesized under autogenous pressure. A mixture of $Co(NO_3)_2{\cdot}6H_2O$, NaN_3, Isonic, LiOH, and H_2O at a ratio of 6:2:2:1:1000 was sealed in a Teflon-lined autoclave, heated to 140 °C for 2 days, and cooled to room temperature at 10 °C h^{-1}. The crystals were obtained in ca. 10% yield based on cobalt. Anal. Calcd for $C_{12}H_{10}Co_3N_8O_6$ (539.07): C, 26.7; H, 1.9; N, 20.8. Found: C, 26.2; H, 2.1; N, 21.1. ***Caution!*** *Azide complexes are potentially explosive. Only a small amount of the materials should be prepared and handled with care.*

(12) Crystal data for **1**: monoclinic, $P2_1/c$, $a = 6.4218(3)$ Å, $b = 18.0665(10)$ Å, $c = 7.8665(4)$ Å, $\beta = 112.1820(10)°$, $V = 845.12(7)$ Å^3, $Z = 2$, λ(Mo Kα) = 0.710 73 Å, 4497 reflections collected, 1568 unique ($R_{int} = 0.0264$), R1 = 0.0274, wR2 = 0.0727 [$I > 2\sigma(I)$]. CCDC No.: 286944.

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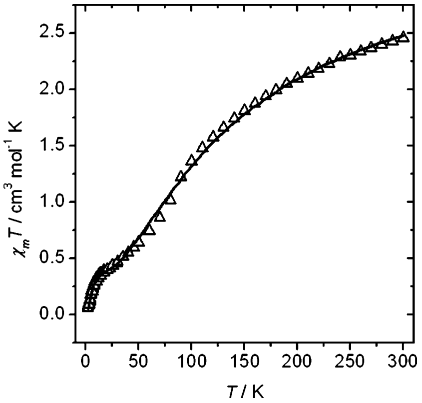

Figure 2. $\chi_M T$ vs T plot for **1**. The solid line indicates the best fit (see the text for the formula used).

entire temperature range are only possible through sophisticated computer programs, based on full-diagonalization methods.[16] 1D systems of Co^{II} are frequently associated with anisotropic Ising systems, and they can be fitted in the low-temperature zone assuming again an effective spin $S' = {}^1/_2$.[17] More recently, Rueff et al.[17c,d] have proposed a phenomenological approach for some low-dimensional Co^{II} systems that allows one to have an *estimate* of the strength of the antiferromagnetic exchange interactions. They postulate the phenomenological equation

$$\chi_M T = A \exp(-E_1/kT) + B \exp(-E_2/kT)$$

in which $A + B$ equals the Curie constant ($\approx$2.8−3.4 cm^3 mol^{-1} K for octahedral Co^{II}) and E_1 and E_2 represent the “activation energies” corresponding to the spin−orbit coupling and the antiferromagnetic exchange interaction. This equation, thus, adequately describes the spin−orbit coupling (high-temperature region) and the exponential low-temperature divergence of the susceptibility. Very good results have been reported in 1D and 2D Co^{II} complexes.[17c,d] In almost all of these complexes, E_1/k, the effect of spin−orbit coupling and site distortion, is on the order of +100 K.[17c,d]

As indicated in the structural part, **1** is a complicated 3D network. However, we can consider the existing 2D entities as quasi-isolated from a magnetic point of view because the linkage among them is only through the long isonicotinate bridging ligand, which can only create a very small, almost negligible, magnetic coupling ($J \approx 0$ cm^{-1}). With this assumption, it is possible to fit the experimental magnetic data using the above-mentioned formula of Rueff and et al.[17c,d]

Thus, applying this formula, we can only give an average J value. The $\chi_M T$ vs T plot for **1** (χ_M is the molar magnetic susceptibility for one Co^{II} ion) is shown in Figure 2. The $\chi_M T$ value at 300 K is 2.5 cm^3 mol^{-1} K. The $\chi_M T$ values of **1** continuously decrease to 0 cm^3 mol^{-1} K at 2 K. From 50 to 2 K, there is a different slope in the curve. At high temperature, the effect of the spin−orbit coupling is manifest, while at low temperatures, the antiferromagnetic coupling is dominant.

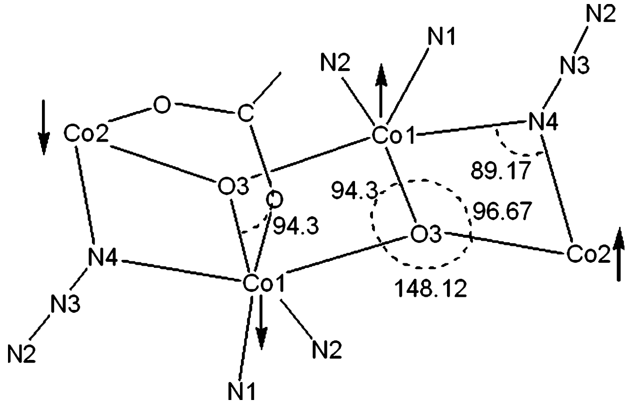

Figure 3. Scheme of the central part of **1** with structural data important from a magnetic point of view. The R−COO bridge on the right part is omitted for clarity. A topology of spins is drawn.

The fit value obtained with the Rueff procedure is $A + B = 3.53$ cm^3 mol^{-1} K, which perfectly agrees with those given in the literature for the Curie constant ($C \approx 2.8-3.5$ cm^3 mol^{-1} K);[17c,d] $E_1/k = 127 \pm 2$ K is of the same magnitude as those reported by Rueff et al. for several 1D and 2D Co^{II} complexes.[17c,d] As for the value found for the antiferromagnetic exchange interaction, it is noticeable ($E_2/k = 4.5$ K), corresponding to $J = -9$ K, according to the Ising chain approximation, $\chi_M T \propto \exp(J/2kT)$.

The 2D network has many magnetic pathways (Figure 3): The Co1−O3−Co2 pathway is predominant and antiferromagnetic because of the high value of the angle (148.12°). The Co2−O3−Co1−N4 moiety will *likely* be ferromagnetic owing to the azido bridge in EO geometry,[3] although the oxo and syn−syn carboxylato bridges will diminish the J value. The Co1−O3−Co1 one could be ferro- or antiferromagnetic because of the value of the angle (94.3°) close to 90°. If this pathway was antiferromagnetic, spin frustration could be a significant feature of the entity. All Co1−(N3)$_2$−Co1 (EE, $\mu_{1,3}$ through N2) pathways will be antiferromagnetic but weak owing to its nonplanarity.[3]

In summary, a new 3D azido-bridged coordination polymer exhibiting a new 3,6-connected net topology was obtained, and its magnetic properties were studied. It is the first metal azide complex with isonicotinate as a bridging coligand.

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Supporting Information Available: X-ray crystallographic data in CIF format, coordination and linkage modes of ligands and Co^{II} ions in **1**, schematic view of the 3,6-connected network topology, and table of select bond lengths of **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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