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Hydrothermal Synthesis and Structure of a Three-Dimensional Cobalt(II) Triazolate Magnet

Wayne Ouellette,[†] José R. Galán-Mascarós,[‡,§] Kim R. Dunbar,[‡] and Jon Zubieta*,[†]

Department of Chemistry, Syracuse University, Syracuse, New York 13244, and Department of Chemistry, Texas A&M University, College Station, Texas 77843

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The reaction of $CoCl_2 \cdot 6H_2O$, 1,2,4-triazole, and H_2O at 200 °C for 96 h yields purple rods of $[Co_2(trz)_3Cl]$ (**1**; trz = 1,2,4-triazolate) in 90% yield. The structure of **1** consists of $\{Co(trz)_3\}_n^{n-}$ chains of Co^{II} sites linked through tetrahedral sites of $\{CoN_3Cl\}$ geometry into a three-dimensional framework. The competing antiferromagnetic interactions of the octahedral and tetrahedral Co^{II} centers result in weak ferromagnetic behavior below $T_c = 9$ K.

Among new classes of materials enjoying widespread contemporary interest, hybrid organic–inorganic materials occupy a prominent position by virtue of their applications to catalysis,[1] optical materials,[2] membranes,[3] and sorption.[4] The diversity of properties associated with these materials reflects a vast compositional range, which allows variations in covalency, geometry, and oxidation states, and a versatile crystalline architecture, which may provide different pore structures, coordination sites, or juxtapositions of functional groups.[5] Furthermore, novel functional materials may be designed by exploiting the electrical, optical, or magnetic properties, mechanical hardness, and thermal stability of the inorganic component and the processability, polarizability, luminescence properties, and synthetic versatility of the organic component.[6,7]

The design of organic–inorganic hybrid materials is conceived of the metal, metal cluster, or metal oxide substructure as a node from which rigid or flexible multitopic organic ligands radiate to act as tethers to adjacent nodes in the bottom-up construction of complex extended architectures. While a variety of organic molecules have been investigated as potential tethers, materials incorporating multitopic carboxylates and pyridine ligands have witnessed the most significant development.[5] However, ligands offering alternative tether lengths, different charge-balance requirements, and orientations of donor groups may afford advantages in the design of materials. One such ligand is 1,2,4-triazole, a member of the polyazaheteroaromatic family of compounds, which exhibit an extensively documented ability to bridge metal ions to afford polynuclear compounds.[8−15] Triazole is an attractive ligand for the design of novel hybrid materials because of the unusual structural diversity associated with the di- and trinucleating properties of the neutral

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* To whom correspondence should be addressed. E-mail: jazubiet@syr.edu. Fax: +(315)443-4070.

[†] Syracuse University.

[‡] Texas A&M University.

[§] On leave from Instituto de Ciencia Molecular, Universitat de Valencia.

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and anionic ligand forms, respectively, a magnetic superexchange capacity reflected in unusual magnetic properties of its complexes, and its facile derivatization to provide bridging ligands with additional functionality. We have also demonstrated that 1,2,4-triazole and its derivatives are stable under hydrothermal reaction conditions, allowing the facile synthesis and crystallization of complex organic−inorganic oxide frameworks with unusual magnetic properties.[16,17] As an extension of these studies, we have begun to explore the hydrothermal chemistry of divalent metal cations with 1,2,4-triazole and its derivatives in materials of the general type $[M_x(trz)_yX_z]$, where X is a structure-influencing anion from the set X = halide, SO_4^{2-}, NO_3^-, etc. The structurally complex and unusual material $[Co_2(trz)_3Cl]$ (**1**; trz = 1,2,4-triazolate) is representative of these new materials.

The hydrothermal reaction of $CoCl_2{\cdot}6H_2O$ and 1,2,4-triazole yields **1** in nearly quantitative yield.[18] Thermal gravimetric analysis (TGA) of **1** under a N_2 atmosphere demonstrates that the material is stable to ca. 470 °C, whereupon the ligand and Cl are lost in two steps (65% weight loss observed; 67% theoretical) to provide an amorphous powder.

As shown in Figure 1a, the structure of **1** is a complex three-dimensional framework with a hexagonal profile when viewed normal to the *bc* plane.[19] The structure is constructed from $\{Co(trz)_3\}_n^{n-}$ chains, running parallel to the crystallographic *a* axis, linked through mononuclear $\{CoN_3Cl\}^+$ units, as illustrated in Figures 1b and 2. Each $\{Co(trz)_3\}_n^{n-}$ chain is connected to six adjacent chains.

There are two distinct Co^{II} environments: the octahedral $\{CoN_6\}$ sites of the chains and the distorted tetrahedral $\{CoN_3Cl\}$ sites, each of which bridges three adjacent chains. Each trz ligand bridges two Co sites of the chain through the N1 and N2 positions and bonds to the tetrahedral Co site through the N4 donor.

The $\{Co(trz)_3\}_n^{n-}$ chains of **1** are similar in profile to the $\{Fe(Htrz)_2(trz)\}_n^{n-}$ chains of $[Fe^{II}(Htrz)_2(trz)](BF_4)$, whose structure was deduced from extended X-ray absorption fine structure data.[20] The Co−Co distance of 3.770(1) Å for **1** is similar to that of 3.63 Å for the Fe^{II} analogue.

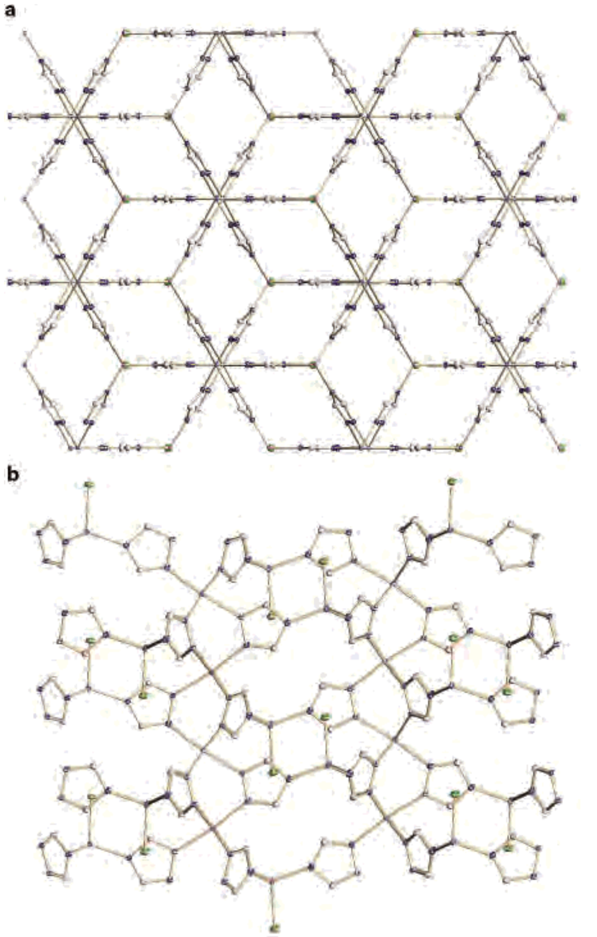

Figure 1. (a) Structure of **1**, viewed normal to the crystallographic *bc* plane and showing thermal ellipsoids at the 50% probability level. Color scheme: purple spheres, Co; green spheres, Cl; light-blue spheres, N; black spheres, C. This scheme is used throughout. (b) View of the structure of **1**, normal to the *ac* plane.

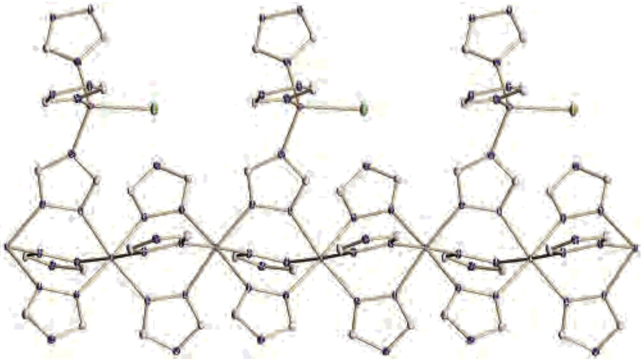

Figure 2. View of the one-dimensional $\{Co(trz)_3\}_n^{n-}$ building block of **1** with one set of tetrahedral $\{CoN_3Cl\}$ sites included to illustrate the connectivity to adjacent chains. When viewed down the crystallographic *a* axis, the trz planes extend outward from the $\{Co(trz)_3\}_n^{n-}$ chain so as to link through the N4 sites to a hexagonal array of tetrahedral Co sites when the structure is projected onto the *bc* plane (see Figure 1a). Thermal ellipsoids are drawn at the 50% probability level.

The magnetic susceptibility measured at 0.1 T (Figure 3) shows a continuous decrease in the χT product with decreasing temperature from a room-temperature value of 5.1 emu·K·mol^{-1}. At 15 K, χT reaches a minimum (2.2 emu·K·mol^{-1}) and then shows a very sharp increase below 10 K. The high-temperature regime can be fitted to a Curie−Weiss model with $C = 5.91$ emu·K·mol^{-1} and $\theta = -47$ K (-32.6 cm^{-1}). The negative sign of the Weiss constant suggests the presence of antiferromagnetic interactions between near neighbors, although the anisotropy of the octahedral Co^{II} centers will also contribute to this value;

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(18) A solution of $CoCl_2{\cdot}6H_2O$ (0.379 g, 1.593 mmol), 1,2,4-triazole (0.235 g, 3.402 mmol), and H_2O (10.00 g, 556 mmol) in the mole ratio of 1.00:2.13:347 was stirred briefly before heating to 200 °C for 96 h. Initial and final pH values of 4.0 and 3.5, respectively, were recorded. Purple rods of **1**, suitable for X-ray diffraction, were collected in 90% yield. IR (KBr pellet, cm^{-1}): 3439(b), 1738(w), 1656(w), 1565(w), 1505(s), 1428(w), 1277(m), 1199(w), 1158(s), 1076(s), 1003(m), 889(w), 866(w), 665(m).

(19) Crystal data for $C_3H_3Cl_{0.5}CoN_{4.5}$: fw 178.75, orthorhombic, *Pnma*, $a = 7.4914(5)$ Å, $b = 9.9397(7)$ Å, $c = 17.381(1)$ Å, $V = 1294.2(2)$ Å, Z = 8, $D_{calc} = 1.835$ g·cm^{-1}, μ(Mo Kα) = 2.765 mm^{-1}, R1 = 0.0293, wR2 = 0.0681 (1691 reflections).

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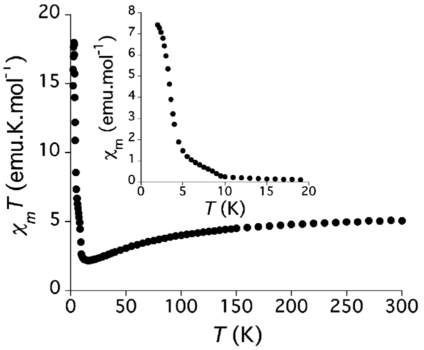

Figure 3. Thermal dependence of the χT product and χ (inset) for **1**.

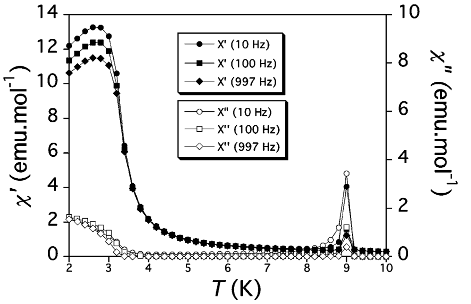

Figure 4. ac magnetic susceptibility for **1**.

therefore, θ is slightly overestimated. In general, the triazole or trz ligand favors weak antiferromagnetic interactions for all of the reported bridging modes.[21] The increase at low temperature suggests the onset of magnetic ordering, arising from the uncompensated antiferromagnetic alignment of the spins. This can be understood from orbital and topological considerations. The isotropic tetrahedral Co^{II} and anisotropic octahedral Co^{II} centers have very different configurations; therefore, the magnitudes of their magnetic moments will not be identical, and antiferromagnetic alignment will not result in a full cancellation of the magnetic moment. In addition, as described in the structural part, the trz ligand connects three Co^{II} centers in a triangular fashion. Although the three interactions are not identical, the triangular array of odd-spin moments precludes the possibility of a diamagnetic ground state. Therefore, compound **1** orders as a weak ferrimagnet.

The presence of magnetic ordering is confirmed by the ac magnetic data (Figure 4), which exhibit a sharp peak in the in-phase magnetic susceptibility, χ', at 9 K, where the out-of-phase susceptibility, χ'', becomes nonzero, defining T_c. Below 5 K, χ' increases again to show a very round maximum at 4 K. The χ'' signal becomes nonzero again at 3.5 K, showing a continuous increase below this temperature. No frequency dependence was observed for any of these features. Therefore, this second maximum should not be due to dynamic effects in the sample but to the onset of a second magnetic transition. Although we cannot assign the origin of the second transition, it may be related to the presence of frustration in the system, as previously described.

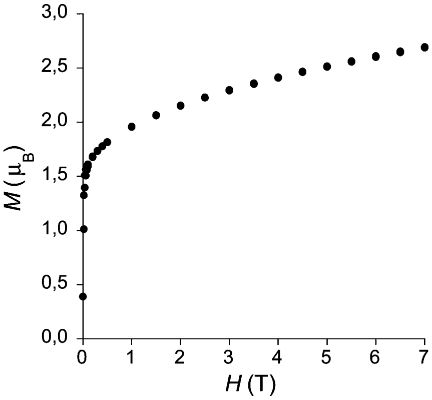

Figure 5. Field dependence of the magnetization at 2 K for **1**.

The field dependence of the magnetization at 2 K (Figure 5) is typical for a weak ferrimagnet, with a very sharp increase at low fields, reaching a value of 1.6 μ_B at 0.1 T (far from the expected saturation value for parallel alignment of all spins) followed by a small but continuous increase for higher fields. There is a very small hysteresis loop of 6 mT.

In summary, compound **1** represents only the second example of a triazole-based magnet[22] and the first case where all three N donor positions are involved in coordination, which increases the dimensionality of the system. This binding mode is also responsible for the presence of triangular arrays of spins, which ensures a magnetic ground state, even when all interactions between near neighbors are antiferromagnetic. It is also noteworthy that the presence of both tetrahedral and octahedral Co^{II} sites creates different magnitudes for the local magnetic moments, despite the exclusive presence of Co^{II} cations. The possible extension of this work to other metals is in progress, with special interest in the Fe^{II} derivatives, where magnetic-ordering and spin-transition phenomena could coexist.

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Supporting Information Available: Crystallographic files in CIF format for compound **1**, experimental procedures of the synthesis of **1**, ORTEP view of a portion of the structure of **1**, TGA profile for **1**, and the hysteresis loop of the magnetization of **1** at 2 K. This material is available free of charge via the Internet at http://pubs.acs.org.

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