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A Cyano-Bridged $Cr^{III}Co^{II}$ Ferromagnet with a Chiral Nanotubular Structure Constituted of Interlocked Single and Double Helices

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We have synthesized an unprecedented 3D cyano-bridged $Cr^{III}-Co^{II}$ compound that self-assembles into a periodically ordered, homochiral interlocking structure composed of left-handed single helices and right-handed double-helical strands. It displays four-connected $6^4 8^2$ chiral networks and exhibits ferromagnetic order below 12 K. The formation of the helical structure results in the creation of helical tubular channels in the crystal.

There has been great interest in the study of new functional compounds with unique and intriguing topologies. Many molecular architectures with novel modes of interconnection, such as helices, rotaxanes, catenanes, and kagome lattices, have been synthesized.[1−3] In particular, the preparation of new functional materials with nanotubular structure has recently received great attention.[4−8] A typical example of such a material is the carbon nanotube, which is currently the subject of many investigations.[9] Furtheremore, inorganic oxide and coordination polymer nanotubes are emerging as attractive materials.[10−14] An important challenge in this field is the preparation of such a chiral tubular structure and the controlled assembly of the tubular units into a multitubular array. Several techniques have been reported on the construction of aligned nanotubes.[13,14]

To date, a few cyano-bridged chiral magnets with a higher magnetic ordering temperature have been prepared based on a well-known synthesis approach by the reaction of hexacyanometalate $[M^{III}(CN)_6]^{3-}$ with coordinatively unsaturated transition-metal complex $[M'L^*]^{m+}$ (L^* = chiral coligands).[15] Especially, Inoue et al. reported a chiral magnet where 6_3-screwed triple-helical chains constructed by Mn^{II} and NH_2ala (D- or L-aminoalanine) were further linked by $[Cr^{III}(CN)_6]_3$ to form a three-dimensional (3D) structure.[15a] Theoretically, 3D-ordered helical and chiral tubular structures could be directly obtained by using hexacyanometalate $[M(CN)_6]^{n-}$ and a coordinatively unsaturated complex. As shown in Scheme 1, when the M−CN−M′−NC−M structure extends in the order of the *y*, *x*, *z*, *y*, *x*, *z*, *y*, ... direction, a 3_2 helical structure can be formed (Scheme 1, left). Furthermore, it is potentially possible to construct an unprecedented structure in which the helices are interlocked in a 3D fashion (Scheme 1, right). Although the connection mode is unusual, through exploration of the preparation methods, here, we reported such an intriguing structure via spontaneous resolution: $[\{Co(L-N_3O_2)\}_2Cr(CN)_6][ClO_4]\cdot 8H_2O$ (**1**)[16] self-assembles to form a periodically ordered nanotubular structure composed of left-handed single helices and right-handed double-helical strands. Compared with other rare examples of the interweaving of different helical ribbons,[17] this unusual entanglement between the helical chains in this

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(16) $C_{18}H_{29}Cl_{0.5}CoCr_{0.5}N_6O_8$, $M_r = 560.13$, trigonal, space group $P3_221$, $a = 16.0231(2)$ Å, $b = 16.0231(2)$ Å, $c = 18.5200(3)$ Å, $\gamma = 120°$, $V = 4117.79(10)$ Å^3, $Z = 6$, $\rho_{calcd} = 1.355$ mg m^{-3}, $\mu = 0.909$ mm^{-1}, $F(000) = 1743$, λ(Mo Kα) $= 0.710\,73$ Å, 5608 unique reflections, 4971 observed reflections [$I \geq 2\sigma(I)$]. R1 = 0.0860 and wR2 = 0.2248 (all data). GOF = 1.065 based on 316 parameters and $\langle E^2 - 1 \rangle = 0.761$ (expected 0.968 for centrosymmetric structure and 0.736 for non-centrosymmetric structure). The structure was solved and refined using the *SHELX-97* program. CCDC 684646 contains the supplementary crystallographc data for this paper, which can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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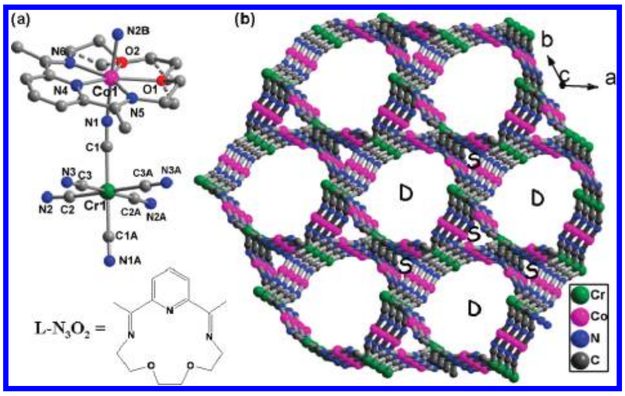
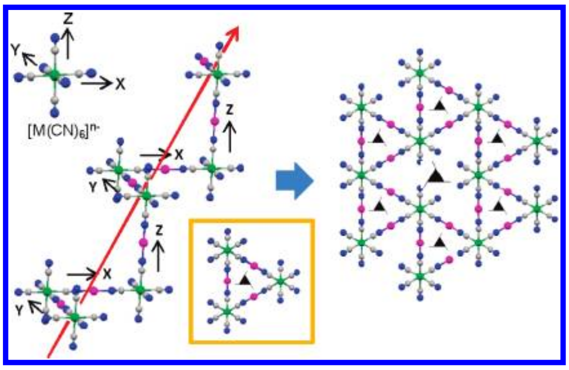


Figure 1. (a) View of the ball-and-stick structure of an asymmetric unit of **1**, where L$-$N$_3$O$_2$ is partly disordered. (b) Chiral 3D tubular network down the *c* axis interlocked by single or double helices. (Only bridging cyanide and corresponding metallic ions are reserved for clarity.)

Scheme 1. [a]



[a] M = green; C = gray; N = blue; M′ = purple.

complex may represent the most effective extending mode of helicity to date, as well as the first example of a cyano-bridged magnetic chiral helical compound derived from achiral components.

Complex **1** was synthesized by mixing K$_3$Cr(CN)$_6$, LiClO$_4$, and [Co(L$-$N$_3$O$_2$)(H$_2$O)$_2$][ClO$_4$]$_2$ (see the Supporting Information, SI). The azaoxamacrocycle ligand (L$-$N$_3$O$_2$) with five basal donors [N$_3$O$_2$] is a bulky ligand.[18] Hence, it is expected that 6-connectivity of [Cr^{III}(CN)$_6$]$^{3-}$ would be prevented as a result of steric hindrance. X-ray crystallographic analysis reveals that **1** shows a novel 3D polymeric assemblage in the chiral space group *P*3$_2$21, interlocked by cyano-bridged Cr^{III}$-$Co^{II} single-helical chains (**S**) or double-helical chains (**D**) (Figure 1). The asymmetric unit consists of half of [Cr(CN)$_6$]$^{3-}$, one [Co(L$-$N$_3$O$_2$)]$^{2+}$ entity, half of ClO$_4$$^-$ as a counteranion, and four lattice water molecules, where both Cr and Cl atoms lie on the 2-fold axes. The Cr^{III} center displays an octahedral coordination geometry with Cr$-$C bond lengths from 2.055(7) to 2.083(7) Å. The Co^{II} site has a pentagonal-bipyramidal environment, consisting of the [N$_3$O$_2$] donor set of the macrocycle forming the basal plane and the two N atoms of the bridging cyanide ligands occupying the apical positions. The Co$-$N/O bond lengths and N/O$-$Co$-$N/O angles in the basal plane vary from 2.101(6) to 2.315(7) Å and from 70.3(4) to 74.2(4)°, while the Co$-$N$_{\text{cyanide}}$ ones are a little shorter, 2.066(6) and 2.088(7) Å. The Co$-$N$\equiv$C bonds deviate distinctly from linearity with angles of 156.6(7) and 158.9(6)°. The resulting apical N1$-$Co1$-$N2B angle is 171.9(3)°. Each [Cr(CN)$_6$]$^{3-}$ unit is linked to four [Co^{II}(L$-$N$_3$O$_2$)]$^{2+}$ moieties by three equatorial and one axial cyanide groups, while the left two CN groups in cis positions are intact, giving a Cr$\cdots$Co separation of 5.15 Å. Correspondingly, each [Co^{II}(L$-$N$_3$O$_2$)]$^{2+}$ links two Cr units. Hence, the assemblage of [Cr(CN)$_6$]$^{3-}$ and [Co^{II}(L$-$N$_3$O$_2$)]$^{2+}$ generates a 3D network with unusual topology possessing the Schäfli symbol of $6^4 8^2$ with long vertex symbol $6^2.6^2.6.6.8^7.8^4$.[19] Each Cr center is considered as a node, and the Co part and the corresponding CN bridges are linear spacers; thus, each Cr node is linked to four others, forming four six-membered and two eight-membered circuits at each metal atom (Figure S1 in the SI). The lattice water molecules and counterbalancing ClO$_4$$^-$ anions reside in these channels of the network, while rich hydrogen bonds are formed between them and the terminal cyano N atoms (Figure S2 in the SI). Indeed, the solvent-accessible void in the framework, as calculated by *PLATON*,[20] in the absence of all water molecules is estimated to be 1148.6 Å^3 per unit cell volume (4117.8 Å^3), representing 27.9% of the potential void per unit volume. Thermogravimetric analysis indicates that **1** is stable up to 220 °C (Figure S3 in the SI), while the first weight loss of 10.0% from room temperature to 115 °C corresponds to the loss of all of the guest water molecules (calculated 12.8%).

The most striking feature of the framework of **1** is the coexistence of both **S** and **D** infinite helices and their unique interlocking mode. Both of the helices are based on repeated [Cr$-$CN$-$Co$-$NC$-$Cr]$_n$ units. The single helix is left-handed along the crystallographic 3$_2$ screw axis parallel to the *c* axis with a helical pitch of 18.5 Å, while the double helices consist of two equal coaxial right-handed helical chains intertwined with each other and possess a pseudo-6$_2$ screw axis along the *c* axis with a pitch of 37.0 Å (Figure S4 in the SI). Another interesting aspect of the present compound is that its single and double helices are derived from each other, suggestive of a similar relevant relationship between three- and six-membered rings in a Kagome lattice.[21] When more carefully looked at, the interlocked single- and double-helical fragments, which share Cr atoms in the entire structure, allowed us to understand the complicated framework in **1**. Six neighboring interlocked single helices in one helical period generate one double helix (Figure S5 in the SI); correspondingly, three adjacent interlocked double helices lead to one single helix inside them (Figures 2a and S6 in the SI). Thus, each single helix is further interlocked to three adjacent ones to give a periodically ordered 3D chiral architecture (Figure 2b), which can also be described as the interlocking of double helices, where each double helix is further interlocked to six adjacent ones by sharing Cr atoms. In other words, the structure can be rationalized as either the interlocking of single-helical chains or that of double-helical chains independently, which is unprecedented. Remarkably, compared with other rare examples of interweaving of different helical ribbons,[17] this unusual entanglement between

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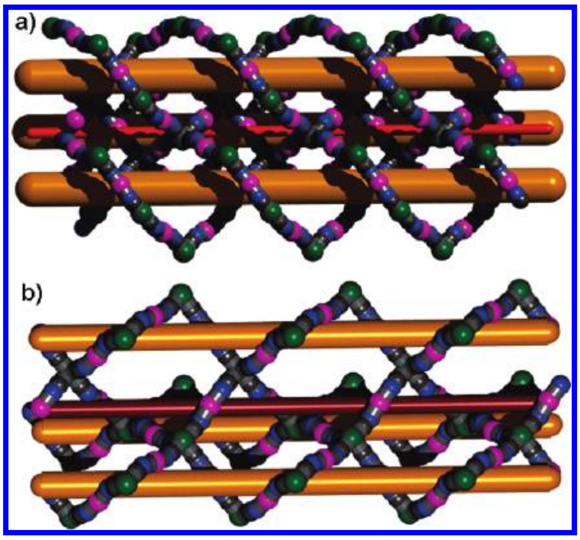

Figure 2. View of the ball-and-stick structures of (a) the interlocking of three neighboring right-handed double helices and (b) the interlocking of four neighboring left-handed single helices, along the *c* axis. (Only metallic ions and corresponding cyanide bridges are included for clarity.)

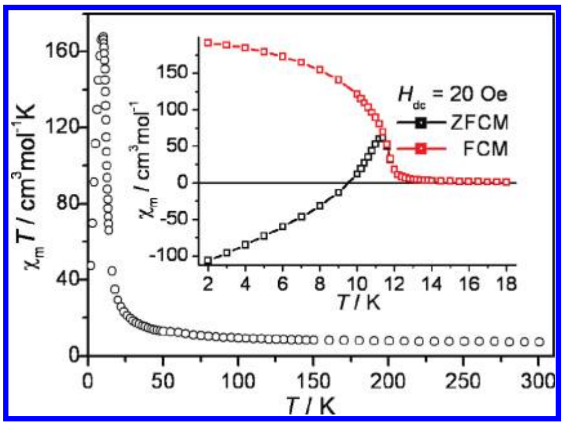

Figure 3. $\chi_M T$ vs T in an applied field of 1 kOe for **1**. Inset: temperature dependence of magnetization at 20 Oe: ZFCM (black □) and FCM (red □).

the helical chains in this complex may represent the most effective extending mode of helicity to date as well as the first example of cyano-bridged chiral helical compounds derived from achiral components. It should also be noted that the formation of single- and double-stranded helical coordination polymers directed by unique bridges is here first obtained. The formation of this unique structure may be due to the special four-connected linkage mode of $[Cr(CN)_6]^{3-}$, which obviously results from the large spatial hindrance of the big azaoxamacrocycle $L-N_3O_2$.

Variable-temperature magnetic susceptibility of **1** (per $[CrCo_2]$ unit) measured at 1 kOe is shown in Figure 3. The $\chi_M T$ value of ca. 7.12 cm^3 mol^{-1} K at 300 K is much higher than the spin-only value of 5.625 cm^3 mol^{-1} K for one low-spin Cr^{III} and two high-spin Co^{II} ions, indicating significant orbital contributions of the heptacoordinated Co^{II} ions.[22] The $\chi_M T$ value increases slowly with decreasing temperature to 50 K, then rapidly reaches a maximum at 10 K, strongly suggesting the occurrence of ferromagnetic (*F*) magnetic order, and then decreases abruptly, possibly being attributed to the presence of zero-field splitting and/or the field-saturation effect. The data above 70 K obey the Curie–Weiss law with a Weiss constant (θ) of +31.0 K, which indicates *F* coupling between the adjacent Co^{II} and Cr^{III} ions. On the basis of the simple molecular field theory, the magnetic exchange coupling constant (J) between cyano-bridged $Co^{II}-Cr^{III}$ ions was estimated to be 1.2 cm^{-1}, which is consistent with the previous estimations.[23]

Both zero-field-cooled magnetization (ZFCM) and field-cooled magnetization (FCM) at an applied field of 20 Oe showed an abrupt increase at 12 K (inset of Figure 3), where out-of-phase (χ_M'') values of the ac susceptibilities appeared. All of these observations strongly confirmed long-range *F* magnetic order below 12 K (Figure S7 in the SI). A pronounced magnetic hysteresis loop at 1.8 K is observed with a remnant magnetization of 4.5 Nβ/mol and a coercive field H_c = 165 Oe, indicating that **1** is a hard ferromagnet below the blocking temperature. It should be noted that the cyano-bridged Cr–Co assemblies, especially 3D ones, are quite rare.[23–25] Especially, the linkage isomerism from $Cr^{III}-CN-Co^{II}$ to $Cr^{III}-CN-Co^{II}$ makes crystallization hard in this system. This study demonstrated that $L-N_3O_2$ may be a promising coligand to stabilize low-charged metallic ions, such as Co^{II}, Fe^{II}, etc., lead to a high-spin state, and prohibit the occurrence of the linkage isomerism.

Considering that carbon nanotubes exhibited some special physical properties, such as metallic or semiconducting properties, enantioselective recognition, and separation, depending on the spiral alignment, it is expected that the title compound might be a potential multifunctional material because of its large tubular porosity, helical and chiral characteristics, and ferromagnetic order. No circular dichroism spectrum for **1** was observed at room temperature, indicating that this material is racemic.

In summary, we have described a cyano-bridged $Cr^{III}-Co^{II}$ compound that self-assembles into a periodically ordered, homochiral nanotube array structure composed of left-handed single helices and right-handed double-helical strands. It displays special four-connected 6^48^2 chiral networks. Compound **1** represents the first example of a cyano-bridged ferromagnet with chiral helical structure derived from achiral components.

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Supporting Information Available: X-ray structural data in CIF format, experiment procedure, IR, TGA, PXRD, and additional magnetic data of **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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