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Cyanide-Bridged W^V–Co^{II} Double-Zigzag Chain Based on an Octacoordinated W Precursor: Metamagnetism and Spin Canting

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A cyanide-bridged W–Co bimetallic complex (**1**) with a double-zigzag chain structure was characterized in terms of structure and magnetism. Compound **1** exhibits metamagnetism and spin canting induced by the presence of anisotropic Co^{II} ions and noncovalent interactions.

Molecule-based magnetic materials have attracted extensive attention because of their potential applications in magnetic devices. They have also shown exotic magnetic characteristics in single-molecule magnets,[1] single-chain magnets,[2] and hybrid magnetic materials. In particular, the construction of multifunctional magnetic assemblies, which contain chiral magnets,[3] photomagnets,[4] porous magnetic systems,[5] and magnetic complexes with blended properties (spin canting/metamagnetism, spin canting/spin flop, etc.),[6] is attained by molecular approaches to combining building units with essential properties via self-assembly processes.

To design such systems, it would be beneficial if a bridging ligand had structural and magnetic predictabilities. Cyanide is one of the good candidates as a bridge for magnetic entities because it links paramagnetic centers in a linear fashion and the magnetic nature of compounds bridged by cyanides is dependent on magnetic orbitals of metal constituents. Cyanide-linked magnetic systems have successfully realized a variety of structures from zero-dimensional to three-dimensional (3D) networks with intriguing multifunctional properties. Recently, because of increasing interest in isolated anisotropic systems, the main emphasis has been on fabricating discrete or one-dimensional (1D) systems to employ molecular precursors with ample coordinating capability, for instance, $[M(CN)_p]^{n-}$ ($p = 6, 8$), and their counterparts having specific vacant sites or labile leaving ligands, $[M'L_xL'_y]^{m+}$ (L = polydentate ligand; L′ = labile group).[7] Another reliable strategy to this aim has been launched by engaging blocked cyanide-based building bricks for low-dimensional materials. The molecular building units with the 3d metal ions, $[M(CN)_pL_q]^{n-}$ (M = Cr^{III}, Fe^{III}), have been thoroughly investigated,[8] while examples, $[M(CN)_pL_q]^{n-}$ (M = Mo^{III}, Re^{II}) that incorporate 4d or 5d metal ions into molecular precursors are still rare to date although the 4d or 5d magnetic orbitals mediate stronger magnetic couplings because they are more diffuse than the 3d magnetic orbitals.[9] We have utilized a new molecular unit $[W(CN)_6(bpy)]^-$ (bpy = 2,2′-bipyridine) as a suitable tecton to produce low-dimensional magnetic systems exhibiting metamagnetism and single-molecule-magnet properties.[10] Our effort to seek systems with the concomitant occurrence of two magnetic characters in one system has been made to locate anisotropic ions in

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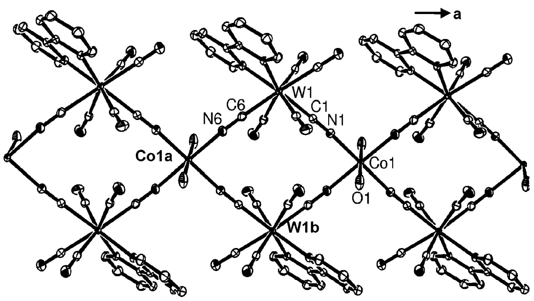

Figure 1. Molecular views of **1** showing the selected atom-labeling scheme. Symmetry code: a $= -1 + x, y, z$; $b = 1 - x, 2 - y, 2 - z$.

molecular assemblies.[11] Herein we report a new 1D W^V−Co^{II} bimetallic coordination polymer, $[W(CN)_6(bpy)]_2[Co(H_2O)_2]\cdot 4H_2O$ (**1**), with double-zigzag chains. This is the first example of the cyanide-bridged 3d−5d bimetallic complexes involving dual magnetic properties of spin canting and metamagnetism that have the capped molecular unit with the 5d metal ion and six CN groups.

A stoichiometric reaction of $(AsPh_4)[W(CN)_6(bpy)]$ in MeCN and $Co(ClO_4)_2\cdot 6H_2O$ in H_2O afforded red crystals of **1** in a yield of 38%.[12] There are no Cl−O stretching vibrations in the IR data for **1**, supporting the completion of the reaction. The characteristic CN peaks are observed at 2165, 2146, and 2119 cm^{-1}. Among them, the band observed at 2165 cm^{-1} can be attributed to bridging CN groups while the rest of the peaks may be responsible for unbound CN groups because the IR peaks of the precursor are visible at 2160w, 2151vw, 2144vw, 2134vw, and 2124vw cm^{-1}.

X-ray analysis reveals that compound **1** crystallizes in the triclinic space group $P\bar{1}$.[12] In the crystal structure (Figure 1), the W^V atom adopts a distorted square-antiprismatic arrangement. The geometric environment consists of six CN groups and one bpy ligand [$W-C_{av} = 2.15(1)$ Å; $W-N_{av} = 2.224(2)$ Å]. The W−CN angle is almost linear, spanning from 171.4° to 178.6°, which is in agreement with those found in octacyanometalate-based bimetallic complexes.[7] The molecular geometry around the Co ion can be viewed as distorted octahedral, comprising four N atoms from bridging CN groups [Co1−N1 = 2.099(2) Å; Co1a−N6 = 2.166(2) Å; a $= -1 + x, y, z$] and two O atoms from coordinated water molecules [Co1−O1 = 2.045(2) Å]. Two among six CN groups of $[W(CN)_6(bpy)]^-$ are coordinated to two Co ions, forming a four-membered square grid of W_2Co_2 with distances of 5.3918(4) Å for W1−Co1, 5.2418(4) Å for W1−Co1a, 8.3504(6) Å for Co1−Co1a, and 6.5853(5) Å for W1−W1b (b $= 1 - x, 2 - y, 2 - z$). The Co−NC angles in the bridging pathways are 174.1(2)° for Co1−N1−C1 and 150.91(19)° for Co1a−N6−C6, which is more linear than those of the W−Mn chain complex.[10a] The extended overall structure can be described as a neutral double-zigzag W^V−Co^{II} chain running along the *a* axis. A similar structural pattern is also found in $[Fe^{III}(CN)_4L]_2[M^{II}(H_2O)_2]\cdot 4H_2O$ [L = bpy, 1,10-phenanthroline, 2,2′-bipyrimidine; M = Mn, Co, Cu, Mn] and $[Cr^{III}(CN)_4L]_2[Mn^{II}(H_2O)_2]\cdot 4H_2O$.[2,8]

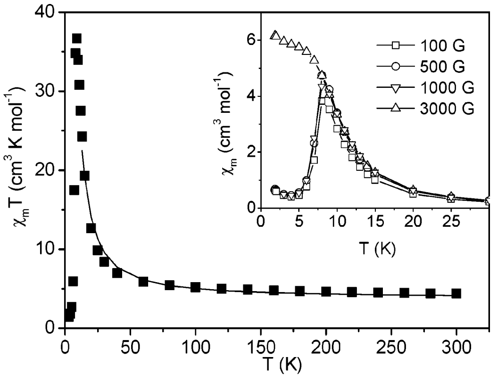

Figure 2. Plot of $\chi_m T$ vs T. The solid line gives the best fit of data with the equation for the alternating chain model. The inset shows the FCMs at indicated fields.

There are two types of appreciable $\pi-\pi$ intermolecular forces between pyridyl rings of bpy ligands in adjacent chains: One (type I) is constructed by the entire overlap of two pyridyl groups of bpy in the range of 3.854−4.168 Å and the other (type II) made up of the contacts of four corresponding pyridyl C atoms on adjacent bpy ligands (3.760−3.865 Å; Figure S1 in the Supporting Information). As a result, the type I contact would play a more dominant role in transmitting magnetic interactions. The extended $\pi-\pi$ interactions eventually bring about a 3D structure. Moreover, the coordinated water molecule (O1) is hydrogen-bonded to the N3 atom of a free CN ligand in the same chain, which has additional hydrogen bonding with a lattice water molecule (O2) and free CN groups (N2 and N5), as well as to the O atom (O3) of a lattice water molecule. Thus, the noncovalent contacts among chains lead to a well-connected 3D supramolecular network. The shortest interchain metal−metal distance in the lattice is 7.5689(6) Å for W−W.

The cryomagnetic properties were measured at 0.1 T in the temperature range of 1.8−300 K. Figure 2 shows the plot of $\chi_m T$ vs T per $W^V_2Co^{II}$ of **1**. The $\chi_m T$ value of 4.41 cm^3 K mol^{-1} at 300 K is larger than the spin-only one (2.38 cm^3 K mol^{-1}) expected for two independent W^V ($S_W = {}^1/_2$; $g = 2$) and one noninteracting high-spin octahedral Co^{II} ($S_{Co} = {}^3/_2$; $g = 2$) centers, which is due to the orbital contribution of the octahedral Co^{II} ions. As the temperature is lowered, $\chi_m T$ goes on a gradual rise and then increases sharply, reaching a maximum of 36.7 cm^3 K mol^{-1} at 9 K. Below the cusp temperature, a dramatic drop is observed. Fitting the data with the Curie−Weiss law [$\chi_m = C/(T - \theta)$] in the high-temperature region of 60−300 K affords parameters of $C = 4.12$ and $\theta = 20.7$ K. The positive Weiss constant implies the apparent existence of ferromagnetic interactions between W^V and Co^{II} spins mediated by CN bridges.

To probe the exchange coupling, the magnetic data were fitted with an analytical expression based on the spin Hamiltonian $H = -J\sum_i S_i \cdot S_{i+1}$. A best fitting at temperatures from 13 to 300 K gives estimated parameters of $g_{Co} = 2.44$, $g_{W'} = 2.00$, and $J = 12.0$ cm^{-1}.[12] The J value denotes that ferromagnetic couplings between W^V and Co^{II} within a chain

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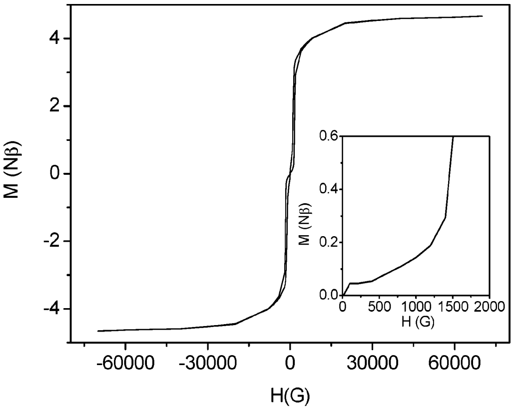

Figure 3. Field dependence of the magnetization (*M*) at fields from −7 to +7 T. The inset denotes a blowup of the magnetization curve at low field.

are operating. The ferromagnetic nature between W^V and Co^{II} ions via CN bridges is consistent with the reported result for a 1D Co−W bimetallic system.[13] The field dependence of the magnetization (M) in the field range from −7 to +7 T is shown in Figure 3. The hysteresis loop is composed of a remnant magnetization of 0.01 Nβ and a coercive field of 10 G. Raising the field engenders a fast saturation of the magnetization, approaching 4.66 Nβ at 7 T. The saturation value concurs with the theoretical range (4−5 Nβ) expected for two W^V ($ngS = 2 \times 2 \times {}^1/_2 = 2$ Nβ) and one Co^{II} (2−3 Nβ) ions,[14] also suggesting the existence of ferromagnetic alignments between W and Co spins. The inset of Figure 3 definitely demonstrates that there are two field-induced magnetic phase transitions at 100 and 1600 G. The first transition appears to be associated with spin canting,[15] which may originate from the local magnetic anisotropy of the Co^{II} ion, whereas the second is typical of metamagnetic behavior. The canting angle is estimated to be ca. 0.6° calculated from the expression $\sin \alpha = M_R/M_S$, where M_R of 0.046 Nβ is deduced from the extrapolation of the linear portion of higher magnetic field to zero field and M_S is the saturation magentization.[16] These phenomena were confirmed by the field-cooled magnetizations (FCMs) at several fields (inset of Figure 2). Below 1600 G, the $\chi_m(T)$ plot clearly signals the presence of antiferromagnetic interactions. When the field increases above 1600 G, the peak disappears, designating a field-induced metamagnetic phase transition from the spin-canted antiferromagnetic state to a ferromagnetic ground state. At low fields and below 4 K, the observation of a slow rise in χ_m pertains to the occurrence of spin canting.[15]

To further inspect the underlying magnetic nature, the measurements of ac magnetic susceptibilities were carried out at zero dc field (Figure S4 in the Supporting Information). The real part (χ_m') of ac susceptibility shows that a maximum is detectable at 8 K, accompanied by a peak at the same temperature in the imaginary component (χ_m''). The observation of a peak in χ_m'' is relevant with spin glasses, single-chain magnets, and long-range ferromangetic orderings. As a result of the appearance of the peak temperature in χ_m'', the existence of an antiferromagnetic ordering at that temperature would be precluded. No frequency dependence in χ_m'' at 8 K and extended intermolecular interactions signify that compound **1** is not likely to act as a spin glass or a single-chain magnet. One plausible explanation is that a magnetized state in **1** exists because even a 1D chain can exhibit a long-range magnetic ordering when interchain magnetic interactions are significant.[17] From the fact that the critical exponent (β) at 3000 G, defined as $M = M_O(1 - T/T_C)^\beta$, is calculated as 0.126, quite close to the theoretical value ($\beta = {}^1/_8$) for two-dimensional (2D) Ising systems,[12,18] the peak at 8 K is probably the ferromagnetic ordering temperature in the 2D layer formed via strong type I $\pi-\pi$ interactions. Upon a decrease in the temperature, the magnetic layers may experience antiferromagnetic couplings through the type II $\pi-\pi$ forces, which are slightly weaker than the type I interactions, and H bonds. The weak interlayer antiferromagnetic interactions can be readily overcome by applying an external magnetic field above 1600 G, and the magnetization saturates to the ferromagnetic phase at high field. An additional phase transition in the $\chi_m''(T)$ plot is observed at 4 K, which may be responsible for spin canting.

In summary, we have prepared a new 1D W−Co bimetallic complex (**1**) showing a double-zigzag chain structure. The dual magnetic characters of metamagnetism and spin canting, where noncovalent forces and local anisotropy of Co^{II} take charge, are evidenced in **1**. The new molecular precursor $[W(CN)_6(bpy)]^-$ coupled with anisotropic sources could offer an opportunity to achieve single-molecule magnets or single-chain magnets on the condition of negligible intermolecular magnetic interactions.

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Supporting Information Available: X-ray crystallographic file in CIF format, additional synthetic, structural, and magnetic data for **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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