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Two octacyanometallate based $W^{V}Ni^{II}$ and $Mo^{V}Ni^{II}$ chains with dominant ferromagnetic interactions

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ABSTRACT

The preparation, single-crystal X-ray crystallography and magnetic properties are reported for two single-zigzag chain complexes $\{[W(CN)_8][Ni(imi)_4]\}\cdot Bu_4N\cdot CH_3OH\cdot 2H_2O$ (**1**) and $\{[Mo(CN)_8][Ni(imi)_4]\}\cdot Bu_4N\cdot 2H_2O$ (**2**) (imi = imidazole, Bu = normal-butyl). The structure studies reveal that both complexes feature one-dimension anion chains linked by $[W(CN)_8]^{3-}$ units in **1** or $[Mo(CN)_8]^{3-}$ units in **2**. Magnetic studies show that strong ferromagnetic exchange is operative within the $W^{V}(\mu\text{-}CN)Ni^{II}$ units for (**1**) and $Mo^{V}(\mu\text{-}CN)Ni^{II}$ units for (**2**).

Single-chain magnets (SCMs) profiting from the slow magnetic relaxation have been explored with tremendous interest for applications in information storage devices and sensing material [1–3]. Since the first experimental one-dimensional (1D) systems displaying slow magnetic dynamics were reported in 2001 by D. Gatteschi and coworkers, many new experimental systems have been developed [4,5]. Recently, chains exhibiting SCM behavior and light-induced phase transition have been reported [6,7]. To obtain the SCMs, a substantial intrachain exchange interaction and negligible magnetic interactions between the chains were desired [8]. Most of the SCMs were synthesized with 3d metal ions as spin carriers, wherein the magnetic interaction is relatively weak through super exchange ways. It is challenging to increase the intrachain magnetic interactions to enhance the blocking temperature of SCMs. It was reported that when 3d spin carriers were superseded by their heavier 4d and 5d congeners, stronger exchange interactions in the molecular magnet have been obtained, because the orbitals of 4d/5d metal ions possess greater diffuseness and radial distribution compared with 3d orbitals. For instance, the exchange strength with Ni^{II} obviously increased following the trend 3d < 4d < 5d in the Cr^{III}, Mo^{V}, and W^{V} cyano-bridged compounds, and the exchange coupling of the W^{V} derivative was twice as large as its 3d homologue Cr^{III} [9]. So the 4d/5d octacyanometalate $[M^{V}(CN)_8]^{3-}$ (M = Mo and W) anions were considered as the good candidates to construct the SCMs. The use of $[M(CN)_8]^{3-}$ (M = Mo, W) anions as the building blocks to design the molecule-based magnetic materials has been particularly productive [10–12], because the Mo and W ions have the excellent characteristics, such as non-zero spin state, variable valence and multiple spatial configurations, e.g., square antiprism (D_{4d}), dodecahedron (D_{2d}) and bicapped trigonal prism (C_{2v}). The octacyanometallate based complexes show rich magnetic properties such as high Curie temperatures, photo-induced magnetism, single-molecule magnetism and single-chain magnetism [13–18].

However, how to use the octacyanometallate building blocks to design and synthesize low-dimensional molecular magnets such as SCMs is still challenging, because the eight cyanides of $[M(CN)_8]^{3-/4-}$ (M = Mo, W) anions were not restricted in the spatial dimension. One reasonable way is to use the organic ligand to occupy parts of coordination sites of the transition-metal ions to form the second building unit (SBU), which further linked the octacyanometallate building blocks to synthesize the low-dimension molecular magnets. With such strategy, we synthesized two one-dimension single-zigzag chain complexes based on $[M(CN)_8]^{3-}$ (M = Mo, W) anions, Ni^{2+} and imidazole. Herein we describe the synthesis, crystal structure, and magnetic properties of the two zigzag chain complexes $\{[W(CN)_8][Ni(imi)_4]\}\cdot Bu_4N\cdot CH_3OH\cdot 2H_2O$ (**1**) (imi = imidazole, Bu = normal-butyl) and $\{[Mo(CN)_8][Ni(imi)_4]\}\cdot Bu_4N\cdot CH_3OH\cdot H_2O$ (**2**).

Complexes **1** and **2** were synthesized by a diffusion method in an H-shaped tube [19]. Single crystal X-ray diffraction analysis revealed that complex **1** crystallizes in a monoclinic $P2_1/c$ space group. **1** consists of an 1D anionic $\{[Ni(imi)_4][W(CN)_8]\}^{-}$ chain, isolated counter cation $[Bu_4N]^{+}$, crystallized methanol and water molecules as shown in Figs. 1(a) and S1(a) [20]. In the chain, two cyanide groups of $[W(CN)_8]^{3-}$ unit bridges two Ni^{II} ions and the other six cyanide

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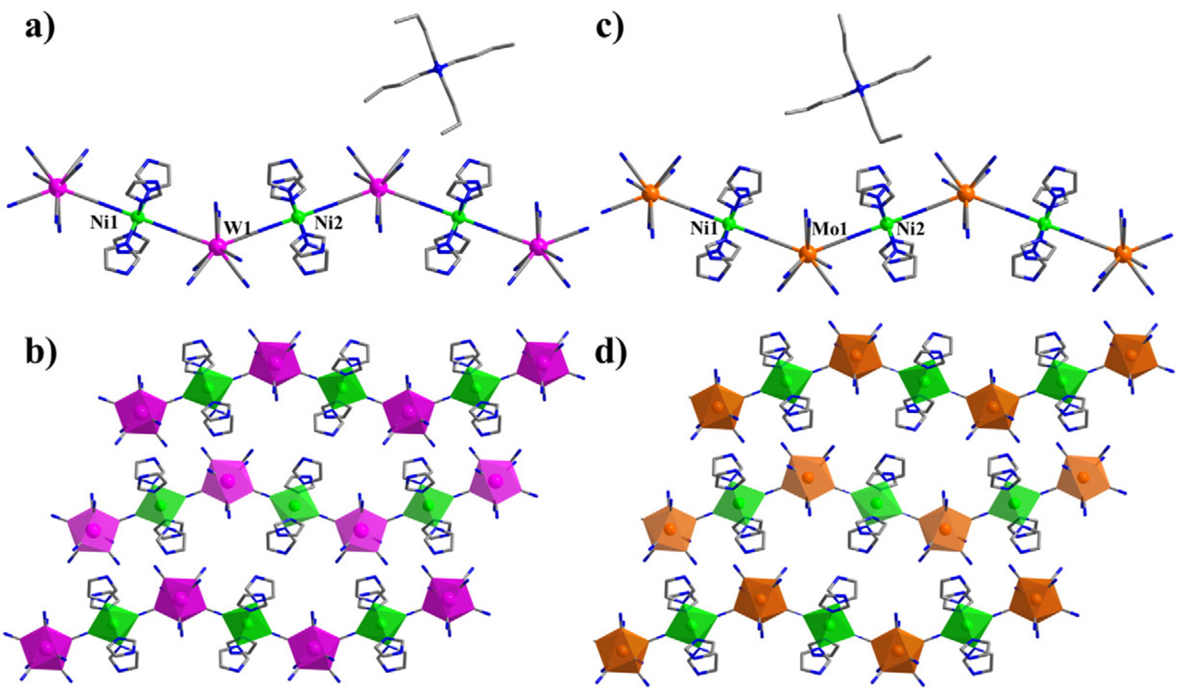

Fig. 1. Perspective view of one-dimensional zigzag infinite chains of **1** (a) and **2** (c) along the *b*-axis. H atoms have been omitted for clarity. (b) Packing diagram of 1D chain of **1** (b) and **2** (d) in the *ac* plane. H atoms, water molecules, methanol molecules have been omitted for clarity. Atomic scheme: W, pink; Mo, orange; Ni, green; C, gray; N, blue; O, red.

groups are free. Each Ni^{II} ion is coordinated to two nitrogen atoms from the CN^{-} and four nitrogen atoms from the imidazole ligand. The coordination geometries of the Ni and W sites are octahedron (D_{4h}) and square antiprism (D_{4d}), respectively. The length of the Ni–N$_{CN}$ coordination bonds were 2.089–2.108 Å and the Ni—N$_{imi}$ bond distances were 2.098–2.119 Å. The W—C bond distances were 2.148–2.170 Å, which were in good agreement with those observed previously in related compounds. The Ni–N–C angles in the bridging linkages are 177.3°–178.7°. The W–C–N linkages are almost linear with angles ranging from 177.3(5)° to 179.3(5)°. The nearest intrachain distance between Ni and W were ca. 5.40 Å, while the nearest intrachain W···W distance is ca. 10.88 Å.

Complex **2** also crystallizes in a monoclinic $P2_{(1)}$/c space group [20]. The crystal structure comprised anionic bimetallic zigzag chains {[Mo(CN)$_8$][Ni(imi)$_4$]}$^{-}$ with Ni(imi)$_4$ repeating units linked by two cyanide bridges of [Mo(CN)$_8$]$^{3-}$, uncoordinated water molecules and [Bu$_4$N]$^{+}$ cations located between them (Figs. 1(b) and S1(b)). The Mo center is coordinated by two bridging and six terminal CN^{-} groups in a distorted square antiprism (D$_{4d}$) with metric parameters typical for the [Mo(CN)$_8$]$^{3-}$ based bimetallic complexes. The average Mo–C and C–N distances are 2.163 and 1.132 Å, respectively. The Mo—C—N bond angles are nearly linear with a maximum deflection of 2.5° from linearity. The Ni centers are in an axially elongated octahedral geometry, in which four nitrogen atoms from imi ligands are located at the equatorial positions with an average Ni–N$_{eq}$ distance of 2.103 Å, while the apical sites are occupied by two nitrogen atoms from bridging cyanide groups of [Mo(CN)$_8$]$^{3-}$ with the mean Ni–N distance of 2.118 Å.

Magnetic measurements were conducted using a superconducting quantum interference device (SQUID) magnetometer (Quantum Design MPMS-7). Variable-temperature magnetic measurements were performed on polycrystalline samples of complex **1** in the range of 1.8–300 K under a dc field of 1000 Oe. As shown in Fig. 2(a), the χT value is 1.69 cm^3 mol^{-1} K per W^{V}Ni^{II} unit at room temperature, being significantly larger than the spin-only value of 1.375 cm^3 mol^{-1} K

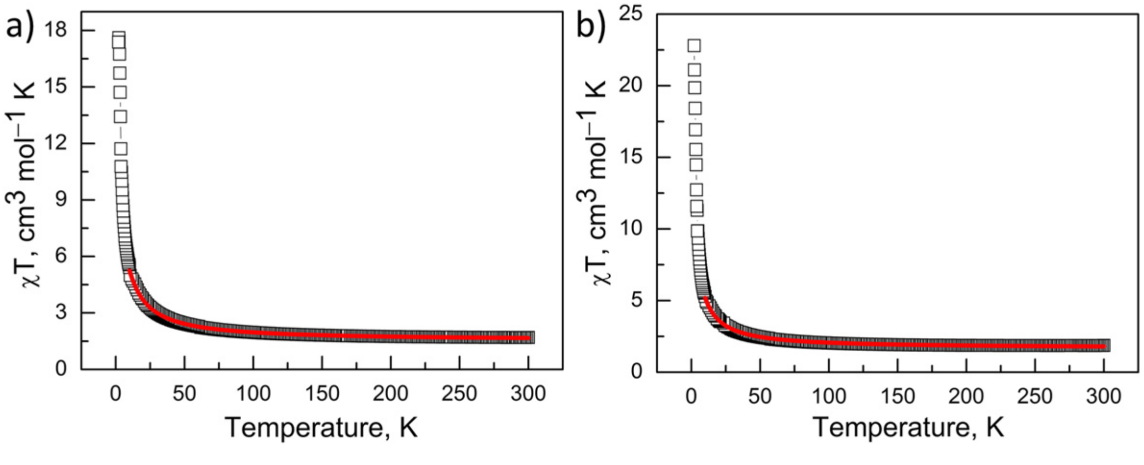

Fig. 2. Temperature-dependent magnetic susceptibility for **1** (a) and **2** (b). The red solid line represents the best fit of the experimental results.