Syntheses, crystal structures, and magnetic properties of Mn–Nb and Co–Nb cyanido-bridged bimetallic assemblies

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Abstract

We report three-dimensional (3D) cyanido-bridged Mn–Nb and Co–Nb bimetal assemblies, $\text{Mn}^{\text{II}}_2[\text{Nb}^{\text{IV}}(\text{CN})_8] \cdot (\text{L})_2 \cdot n\text{H}_2\text{O}$ (**1**: L = 5-aminopyrimidine, n = 5; **2**: L = 5-methylpyrimidine, n = 4), and $\text{Co}^{\text{II}}_2[\text{Nb}^{\text{IV}}(\text{CN})_8] \cdot (4\text{-pyridinealdoxime})_8 \cdot 2\text{H}_2\text{O}$ (**3**). The single-crystal X-ray structural analyses show that **1** and **2** consist of isomorphic 3D cyanido-bridged network (monoclinic, $P2_1/n$) composed of square antiprism Nb sites and distorted octahedral Mn sites. Both **1** and **2** show ferrimagnetism with Curie temperatures (T_C) of 32 and 34 K, respectively, which is caused by the antiferromagnetic superexchange interaction between Mn^{II} ($S = 5/2$) and Nb^{IV} ($S = 1/2$) through the CN groups. **3** has a 3D cyanido-bridged network (tetragonal, $I4_1/a$) composed of a dodecahedral Nb site and axially distorted pseudo-octahedral Co site. This compound shows ferromagnetic ordering with a T_C of 18 K. Magnetization vs rotation angle of single crystal reveals that **3** has a large coercive field of 15000 Oe as crystal is oriented to a -axis, which is due to the strong magnetic anisotropy on distorted Co^{II} .

Keywords: Molecular-based magnet, octacyanidonibate, 3D network, magnetic anisotropy, large coercive field

1. Introduction

The improvement of magnetic properties such as Curie temperature (T_C) and coercive field (H_C) is a significant issue in the field of molecular magnetic materials [1]. The investigation of external stimulation controls is also an attractive issue. Cyanido-bridged bimetal assemblies are suitable systems for these aims, because they potentially exhibit high- T_C values [2] and their magnetic properties can be controlled by molecular adsorption or light irradiation [3,4]. Among cyanido-bridged bimetal assemblies, octacyanidometalate-based assemblies have provided new opto-magnetic functionalities [5], such as light-induced spin-crossover magnetization on $\text{Fe}_2[\text{Nb}(\text{CN})_8] \cdot (4\text{-pyridinealdoxime})_8 \cdot 2\text{H}_2\text{O}$ [4f] and 90-degree optical switching of magnetization-induced second harmonic generation on $\text{Fe}_2[\text{Nb}(\text{CN})_8] \cdot (4\text{-bromopyridine})_8 \cdot 2\text{H}_2\text{O}$ chiral magnet [4h].

To design magnetic properties, e.g. T_C and H_C , the coordination geometries of each metal ion play an important role. For example, octacyanidometalates can take several types of coordination geometries such as dodecahedron, a bicapped trigonal prism, or a square antiprism, and then its bimetallic assemblies also have various crystal structures. From the viewpoint of T_C , divalent manganese ion is useful because of its high spin quantum number ($S = 5/2$), and small-sized monodentate or bridging organic ligands are more preferable than bulky chelating organic ligands as they can give high density packing and high coordination numbers leading to efficient superexchange coupling. Up to date, three-dimensional (3D) octacyanidometalate-based magnets

with relatively high T_C have been synthesized [6]. Furthermore, in the case of octacyanidoniate-based magnets, the T_C value depends on the coordination geometry of $[\text{Nb}(\text{CN})_8]^{4-}$. For example, $\text{Mn}_2[\text{Nb}(\text{CN})_8] \cdot (3\text{-pyridinemethanol})_8 \cdot 2\text{H}_2\text{O}$ based on a square-antiprism type exhibits $T_C = 24$ K, whereas $\text{Mn}_2[\text{Nb}(\text{CN})_8] \cdot (3\text{-aminopyridine})_8 \cdot 2\text{H}_2\text{O}$ based on a dodecahedron type exhibits $T_C = 43$ K [6i]. Such a difference in T_C values can be understood by the electron density on nitrogen atoms of the octacyanidoniate ion. As for the H_c value, it can be influenced by magnetic anisotropy. The magnetic anisotropy of transition metal ion attributes to the electron configuration and coordination environment of metal ion. For example, divalent cobalt ion ($3d^7$) is known to have a strong magnetic anisotropy due to the single-ion anisotropy [4g,7].

In this work, we prepared Mn–Nb and Co–Nb octacyanidometalate-based magnets, $\text{Mn}^{\text{II}}_2[\text{Nb}^{\text{IV}}(\text{CN})_8] \cdot (\text{L})_2 \cdot n\text{H}_2\text{O}$ (**1**: L = 5-aminopyrimidine, n = 5; **2**: L = 5-methylpyrimidine, n = 4), and $\text{Co}^{\text{II}}_2[\text{Nb}^{\text{IV}}(\text{CN})_8] \cdot (4\text{-pyridinealdoxime})_8 \cdot 2\text{H}_2\text{O}$ (**3**). While **1** and **2** show ferrimagnetism, **3** shows ferromagnetism. In particular, **3** shows a large coercive field of 15000 Oe, which is caused by the magnetic anisotropy of the Co^{2+} ion.

2. Experimental

2. 1. Syntheses

$\text{Mn}^{\text{II}}_2[\text{Nb}^{\text{IV}}(\text{CN})_8] \cdot (5\text{-aminopyrimidine})_2 \cdot 5\text{H}_2\text{O}$ (1**).**

We obtained **1** as red crystals by the reaction of a mixed aqueous solution (2 mL) of $\text{Mn}^{\text{II}}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (0.2 mmol), 5-aminopyrimidine (0.4 mmol), and potassium nitrate (1 mmol) with

a mixed aqueous solution (2 mL) of $\text{K}_4[\text{Nb}^{\text{IV}}(\text{CN})_8] \cdot 2\text{H}_2\text{O}$ [8] (0.1 mmol) and potassium nitrate (1 mmol), using a slow diffusion method. Elemental analyses confirmed the formula to be $\text{Mn}_2[\text{Nb}(\text{CN})_8] \cdot (\text{C}_4\text{H}_5\text{N}_3)_2 \cdot 5\text{H}_2\text{O}$. Calcd: Mn, 15.9%; Nb, 13.4%; C, 27.8%; H, 2.9%; N, 28.4%; Found: Mn 16.1%, Nb, 13.4%; C, 28.0%; H, 2.9%; N, 28.3%. The infrared (IR) spectrum showed CN stretching peaks at 2132, 2135, 2139 and 2149 cm^{-1} . The thermogravimetric measurement also supported the formula (Figure S1).

$\text{Mn}^{\text{II}}_2[\text{Nb}^{\text{IV}}(\text{CN})_8] \cdot (5\text{-methylpyrimidine})_2 \cdot 4\text{H}_2\text{O}$ (2).

Compound **2** was obtained as red crystals by the reaction of a mixed aqueous solution (2 mL) of $\text{Mn}^{\text{II}}\text{Cl}_2 \cdot 4\text{H}_2\text{O}$ (0.2 mmol) and 5-methylpyrimidine (1 mmol) with an aqueous solution (2 mL) of $\text{K}_4[\text{Nb}^{\text{IV}}(\text{CN})_8] \cdot 2\text{H}_2\text{O}$ (0.1 mmol) using a slow diffusion method. Elemental analyses confirmed the formula to be $\text{Mn}_2[\text{Nb}(\text{CN})_8] \cdot (\text{C}_5\text{H}_6\text{N}_2)_2 \cdot 4\text{H}_2\text{O}$. Calcd: Mn, 16.4%; Nb, 13.8%; C, 32.2%; H, 3.0%; N, 25.0%; Found: Mn, 16.2%; Nb, 13.9%; C, 32.1%; H, 3.2%; N, 25.0%. The IR spectrum showed CN stretching peaks at 2130, 2138, 2143 and 2153 cm^{-1} . The thermogravimetric measurement also supported the formula (Figure S1).

$\text{Co}^{\text{II}}_2[\text{Nb}^{\text{IV}}(\text{CN})_8] \cdot (4\text{-pyridinealdoxime})_8 \cdot 2\text{H}_2\text{O}$ (3).

Compound **3** was obtained as orange crystals by the reaction of a mixed aqueous solution (2 mL) of $\text{Co}^{\text{II}}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ (0.1 mmol), 4-pyridinealdoxime (1 mmol), L-ascorbic acid (0.3 mmol), potassium acetate (0.1 mmol), and 1,3-propanediamine (0.5 mmol) with an aqueous solution (2 mL) of $\text{K}_4[\text{Nb}^{\text{IV}}(\text{CN})_8] \cdot 2\text{H}_2\text{O}$ (0.05 mmol) and potassium acetate (0.1 mmol), using a slow diffusion method into aqueous solution (16 mL) of potassium acetate (0.8 mmol) in a H-tube.

Elemental analysis was performed using a powder sample. Elemental analyses confirmed the formula to be $\text{Co}_2[\text{Nb}(\text{CN})_8] \cdot (\text{C}_6\text{H}_6\text{N}_2\text{O})_8 \cdot 2\text{H}_2\text{O}$. Calcd: Co, 8.2%; Nb, 6.5%; C, 47.0%; H, 3.7%; N, 23.5%; Found: Co, 8.3%; Nb, 6.5%; C, 47.2%; H, 3.8%; N, 23.6%. The IR spectrum showed CN stretching peaks at 2159 and 2131 cm^{-1} .

2. 2. *Physical measurements*

Elemental analyses of metal ions were performed by Agilent 7700 inductively coupled plasma mass spectroscopy (ICP-MS), whereas those of C, H, and N were conducted using standard microanalytical methods. IR spectra (4000–400 cm^{-1}) were recorded with a JASCO FT-IR4100 spectrometer with the samples in KBr pellets. X-ray structural analyses were performed on a Rigaku R-Axis RAPID imaging plate area detector with graphite monochromated Mo $\text{K}\alpha$ radiation. The structures were solved by a direct method and refined by a full-matrix least-squares technique using SHELXL-97 [9]. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms of 5-methylpyrimidine, 5-aminopyrimidine, and 4-pyridinealdoxime on aromatic rings were refined using the riding model. Water molecules of **3** could not be located with the certainty because of their structural disorder, and they are not included in the refinement.

Thermogravimetric measurements were conducted on a RIGAKU TG-8120 at a heating rate of 2 $^{\circ}\text{C min}^{-1}$. Magnetic measurements were performed using a Quantum Design MPMS superconducting quantum interference device magnetometer.

3. Results and discussion

3.1. Synthesis

Single crystals of **1**, **2**, and **3** were obtained by using slow diffusion method. The elemental analyses for the crystals confirmed the formulas of $\text{Mn}^{\text{II}}_2[\text{Nb}^{\text{IV}}(\text{CN})_8] \cdot (5\text{-aminopyrimidine})_2 \cdot 5\text{H}_2\text{O}$, $\text{Mn}^{\text{II}}_2[\text{Nb}^{\text{IV}}(\text{CN})_8] \cdot (5\text{-methylpyrimidine})_2 \cdot 4\text{H}_2\text{O}$, and $\text{Co}^{\text{II}}_2[\text{Nb}^{\text{IV}}(\text{CN})_8] \cdot (4\text{-pyridinealdoxime})_8 \cdot 2\text{H}_2\text{O}$, respectively. In the synthesis, an excess quantity of organic ligands was used to obtain the compounds with desired stoichiometry and modification of the synthetic conditions, e.g., Mn/Nb/L ratio, examination of counter anion, and addition of 1,3-propanediamine and ascorbic acid were performed to get a good crystallinity.

3.2. Crystal structures

Single-crystal X-ray structural analyses reveal that **1** and **2** have the monoclinic space group $P2_1/n$ with lattice parameters as shown in Table 1. Compound **1** has lattice parameters of $a = 13.0982(5) \text{ \AA}$, $b = 13.2592(5) \text{ \AA}$, $c = 15.4421(6) \text{ \AA}$, $\beta = 95.997(1)^\circ$, $V = 2667.2(2) \text{ \AA}^3$, and $Z = 4$. The asymmetric unit of **1** is composed of a $[\text{Nb}^{\text{IV}}(\text{CN})_8]^{4-}$ anion, two $[\text{Mn}^{\text{II}}(5\text{-aminopyrimidine})(\text{H}_2\text{O})]^{2+}$ cations (Mn1 and Mn2), and three non-coordinated water molecules (so called zeolitic water) (Figure 1a). The coordination geometry around $[\text{Nb}(\text{CN})_8]^{4-}$ is square antiprism, in which six CN groups bridge to Mn, and the other two are free. The Nb–C bond lengths are almost in the same range, indicating that all the CN groups are chemically equivalent (Tables S1 and S2). The two Mn sites (Mn1 and Mn2) adopt six-coordinated distorted octahedral geometries, and the two Mn sites are coordinated to three cyanido nitrogen atoms of $[\text{Nb}(\text{CN})_8]^{4-}$ two nitrogen atoms of 5-aminopyrimidine, and one oxygen atom of the water ligand. The Mn and

Nb are alternately bridged by CN ligands, resulting in a 3D cyanido-bridged network structure (Figure 1b, Table S3). In addition, the 5-aminopyrimidine bridges two Mn sites to sustain the 3D structure. The amino group of 5-aminopyrimidine is not coordinated to metal ion probably due to the weak coordination ability because of the electron delocalization to aromatic ring. In the crystal structure of **1**, there are three kinds of zeolitic water molecules (O3, O4, and O5). The zeolitic water molecules of O3 and O4 make the hydrogen bonds with cyanido nitrogen atoms and coordinated water molecules of O1 and O2. The disordered zeolitic water molecule of O5 forms the hydrogen bonds with a cyanido nitrogen atom, a coordinated water molecule of O1, and an amino group of 5-aminopyrimidine. The hydrogen bonds made by O5 are longer than those produced by O3 and O4 (Table S4).

Compound **2** is isostructural to **1** ($a = 13.1851(3) \text{ \AA}$, $b = 13.2870(3) \text{ \AA}$, $c = 15.4634(4) \text{ \AA}$, $\beta = 95.7077(8)^\circ$, $V = 2695.6(1) \text{ \AA}^3$, and $Z = 4$), containing 5-methylpyrimidine as a bidentate organic ligand (Figure 2, Tables S3, S5 and S6). The asymmetric unit of **2** consists of one $[\text{Nb}^{\text{IV}}(\text{CN})_8]^{4-}$ anion, two $[\text{Mn}^{\text{II}}(5\text{-methylpyrimidine})(\text{H}_2\text{O})]^{2+}$ cations (Mn1 and Mn2), and two zeolitic water molecules (Figure 2). The coordination geometries around Nb and Mn are that of a square antiprism and a distorted octahedron, respectively. In the crystal structure of **2**, the two zeolite water molecules (O3 and O4) form the hydrogen bonds with cyanido nitrogen atoms and coordinated water molecules of O1 and O2 (Table S4). Compared with **1**, one zeolitic water molecule is absent in the crystal structure of **2**. The crystal structures of **1** and **2** indicate that the similarities in size and shape of the ligands lead to isomorphic structures, while the difference in hydrophilicity between

amino group and methyl group is considered to affect the quantity of water molecules in the crystal structures.

The single crystal X-ray structure analysis of **3** shows that the compound has a tetragonal structure in the $I4_1/a$ space group, with $a = 20.1981(9)$ Å, $c = 14.9775(6)$ Å, and $Z = 4$ (Figure 3). Figure 3a shows the asymmetric unit and unit cell of the cyanido-bridged Co–Nb bimetallic framework. The coordination geometries of Nb and Co sites are dodecahedron (D_{2d}) and pseudo-octahedron (D_{4h}), respectively. In the eight CN groups of $[\text{Nb}(\text{CN})_8]^{4-}$, the four CN groups are bridged to Co ions, and the other four CN groups are free. The two axial positions of the Co are occupied by cyanido nitrogen atoms and the other four equatorial positions are occupied by pyridyl nitrogen atoms of 4-pyridinealdoxime, forming a 3D cyanido-bridged network structure (Figure 1b, Table S3, S7, and S8). In the crystal structure of **3**, the hydrogen bonds are formed between the oxygen atom of oxime group of 4-pyridinealdoxime and non-bridging cyanido nitrogen of $[\text{Nb}(\text{CN})_8]^{4-}$, two oxygen atoms of oxime groups of 4-pyridinealdoxime, the oxygen atom of oxime group of 4-pyridinealdoxime and nitrogen atom of oxime group of other 4-pyridinealdoxime (Table S9).

3.2. Curie temperature

The field-cooled magnetization (FCM), zero-field-cooled magnetization (ZFCM), and remnant magnetization (RM) curves for **1** and **2** under an external magnetic field (H_{ex}) of 10 Oe show the T_{C} values of 32 K (**1**) and 34 K (**2**), respectively (Figure 4). The initial magnetization vs external magnetic field plots at 2 K show the saturation magnetization (M_{s}) values of $9.1 \mu_{\text{B}}$ (**1**) and $9.0 \mu_{\text{B}}$

(2) (Figure 5). These M_s values agree well with the theoretical value of $9.0 \mu_B$ for ferrimagnetic ordering between Nb^{IV} ($S = 1/2$) and Mn^{II} ($S = 5/2$), which indicates that **1** and **2** are ferrimagnets. The values of the superexchange interaction constants J_{MnNb} are related to the T_C values via the following equation based on molecular-field theory [10]:

$$T_C = \frac{|J_{\text{MnNb}}| \sqrt{Z_{\text{MnNb}} Z_{\text{NbMn}} S_{\text{Mn}} (S_{\text{Mn}} + 1) S_{\text{Nb}} (S_{\text{Nb}} + 1)}}{3k_B},$$

where S_{Nb} and S_{Mn} are spin quantum numbers ($S_{\text{Nb}} = 1/2$, $S_{\text{Mn}} = 5/2$), Z_{NbMn} and Z_{MnNb} are the coordination numbers of neighboring sites ($Z_{\text{MnNb}} = 3$, $Z_{\text{NbMn}} = 6$), and k_B is the Boltzmann constant. From the T_C values of **1** and **2**, the values obtained were $J_{\text{MnNb}} = -6.1 \text{ cm}^{-1}$ (**1**) and -6.5 cm^{-1} (**2**). These T_C values are comparable to the cyanido-bridged Mn–Nb system based on a square-antiprism $[\text{Nb}(\text{CN})_8]^{4-}$ [6i].

The magnetization vs temperature curves of **3** showed an increase of magnetization below 18 K under $H_{\text{ex}} = 1000 \text{ Oe}$ along the crystallographic c -axis, whereas magnetization was small when the sample was oriented along the a - or b -axis (Figure 6a). The rotation dependence of RM along the ac - or bc -plane corresponds to a sine function with a maximum value along the c -axis and a minimum value along the a - or b -axis, demonstrating that the remnant magnetization of the sample is oriented along the c -axis (Figure 6b, c). In magnetization vs external magnetic field curve at various rotation angles, the magnetization value at 7 T has a maximum of $5.9 \mu_B$ along the c -axis and a minimum of $2.4 \mu_B$ along the a -axis (Figure 7a). In Co^{II} , the ground Kramer's doublet is thermally populated at 2 K. In such cases, the magnetism of Co^{II} is explained by $S = 1/2$ and the

effective g -value $g_{\text{eff}} = 13/3$ [6c]. Using the magnetic moments of two Co^{II} ($13/6 \mu_{\text{B}}$) and one Nb^{IV} ($1 \mu_{\text{B}}$), the estimated M_{s} value of ferromagnetic ordering is $5.3 \mu_{\text{B}}$, and that of ferrimagnetic ordering is $3.3 \mu_{\text{B}}$. The magnetization value of $5.9 \mu_{\text{B}}$ at 7 T indicates a ferromagnetic interaction between magnetic spins on Co^{II} and Nb^{IV} . The superexchange interaction constant (J_{CoNb}) of **3** is calculated from the T_{C} values as $J_{\text{CoNb}} = +17.8 \text{ cm}^{-1}$.

To understand the superexchange interaction of **1–3**, the molecular orbitals of the octacyanidonioate(IV) moiety of **1–3** were calculated using the DV- $X\alpha$ method [11]. Figure 8 shows the energy levels of 4d orbitals and the magnetic orbitals. In the case of **1** possessing square-antiprism $[\text{Nb}(\text{CN})_8]^{4-}$, the magnetic orbital consists of 68.0% $4d_{z^2}$ (Nb), 0.3% 2p (C), and 3.6% 2p (N: bridging CN). The magnetic orbital of **2** possessing square-antiprism $[\text{Nb}(\text{CN})_8]^{4-}$ is made up of 68.0% $4d_{z^2}$ (Nb), 0.3% 2p (C), and 3.7% 2p (N: bridging CN). The difference of the population of 2p (N) between **1** and **2** is considerably small. Because the overlap between 2p (N: bridging CN) and 3d (Mn) causes the superexchange interactions between Nb and Mn, **1** and **2** should exhibit similar T_{C} values. In contrast, the magnetic orbital of **3** with dodecahedral $[\text{Nb}(\text{CN})_8]^{4-}$ is composed of 66.9% $4d_{xy}$ (Nb), 0.4% 2p (C), and 5.7% 2p (N: bridging CN). The population of 2p (N: bridging CN) of **3** is significantly larger than those of **1** and **2**, most likely due to the dodecahedral geometry around $[\text{Nb}(\text{CN})_8]^{4-}$ of **3**. The large 2p (N: bridging CN) population explains the strong superexchange interaction observed in **3**.

3.3 Coercive field

The H_c value of **3** depends on the orientation of the crystal, especially, 15000 Oe is recorded when H_{ex} is applied along the a -axis (Figure 7b). To understand the large coercivity of **3**, the molecular orbitals of the $[\text{Co}(\text{NC})_2(4\text{-pyridinealdoxime})_4]$ unit of **3** were calculated using the DV- $X\alpha$ method [11]. Figure 9 shows the energy levels of the 3d orbitals and the magnetic orbitals of the $[\text{Co}(\text{NC})_2(4\text{-pyridinealdoxime})_4]$ unit. Reflecting the compressed coordination geometry of Co^{II} along the CN–Co–NC direction (D_{4h} symmetry), the d_{xz} and d_{yz} orbitals are almost degenerate. In such cases, a large magnetic anisotropy due to single-ion anisotropy can be expected. In **3**, a large coercive field of 15000 Oe is observed. The single-ion anisotropy generated by the distorted coordination geometry of Co is considered to be due to the observed large coercivity of **3**.

4. Conclusions

In this study, we have prepared three kinds of octacyanido-bridged Mn–Nb and Co–Nb bimetallic assemblies with 3D network structure. Assemblies **1** and **2** consist of isomorphic crystal structures and show ferrimagnetism with T_C of 32 K (**1**) and 34 K (**2**), whereas **3** exhibits ferromagnetism with a T_C of 18 K. The superexchange interaction constants (J) are estimated to be -6.1 cm^{-1} (**1**), -6.5 cm^{-1} (**2**), and $+17.8 \text{ cm}^{-1}$ (**3**). The H_c value of **3** is 15000 Oe along the a -axis. The molecular orbital calculations of **1** and **2** with square-antiprism Nb sites show similarity to magnetic orbitals of $[\text{Nb}^{\text{IV}}(\text{CN})_8]^{4-}$, suggesting similar T_C values, while assembly **3**, with dodecahedron Nb sites, has a larger population on 2p orbitals of the N atoms of bridging CN, supporting a larger superexchange interaction. The molecular orbital calculation of $[\text{Co}(\text{NC})_2(4\text{-pyridinealdoxime})_4]$ moiety indicated

degenerate magnetic orbitals of the Co^{II} center, which suggests a large magnetic anisotropy due to single-ion anisotropy.

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Table and Figure captions

Table 1 Crystallographic data of **1**, **2**, and **3**.

Figure 1 Crystal structure of **1**. (a) Asymmetric unit, and view of the cyanido-bridged Mn–Nb three-dimensional framework along (b) the *a*-axis, (c) the *b*-axis, and (d) the *c*-axis. Green, purple, dark gray, gray, and blue balls represent Nb, Mn, C, N, and O, respectively. Red ball shows a disordered zeolitic water molecules. All hydrogen atoms are omitted for clarity.

Figure 2 Crystal structure of **2**. (a) Asymmetric unit, and view of the cyanido-bridged Mn–Nb three-dimensional framework along (b) the *a*-axis, (c) the *b*-axis, and (d) the *c*-axis. Green, purple, dark gray, gray, and blue balls represent Nb, Mn, C, N, and O, respectively. All hydrogen atoms are omitted for clarity.

Figure 3 Crystal structure of **3**. (a) The coordination environments around Co^{II} and Nb^{IV}. (b) The bimetallic framework of cyanido-bridged Co^{II}–Nb^{IV} ions viewed from the *b*-axis, (c) the *a*-axis, and (d) the *c*-axis. Green, red, brown, light blue, and pink balls represent Nb, Co, C, N, and O atoms, respectively. All hydrogen atoms are omitted for clarity.

Figure 4 Field-cooled magnetization (FCM) (red), zero-field-cooled magnetization (ZFCM) (black), and remnant magnetization (RM) (blue) curves for (a) **1** and (b) **2** in an external magnetic field of 10 Oe.

Figure 5 Initial magnetization vs external magnetic field curves of (a) **1** and (b) **2** at 2 K.

Figure 6 Magnetic properties of **3** measured with one single crystal. (a) Magnetization vs temperature curve under the external field of 1000 Oe applied along each axis. (b) Rotation dependence of remnant magnetization in *ac*-plane and (c) *bc*-plane. (d) Description of magnetic easy and hard axes in the crystal structure.

Figure 7 Magnetization vs external magnetic field curve of **3**. (a) Rotation dependence of initial magnetization curve along *ac*-plane at 2 K. (b) Rotation dependence of magnetic hysteresis along *ac*-plane at 2 K. Red, pink, orange, green, light green, light blue, and blue plots represent the magnetization value when external magnetic field is applied 0°, 15°, 30°, 45°, 60°, 75°, and 90° with respect to *c*-axis.

Figure 8 Energy levels and magnetic orbitals of octacyanidonioate(IV) moiety of (a) **1**, (b) **2**, and (c) **3** calculated using DV-X α program.

Figure 9 Energy levels of Co^{II} 3d orbitals and degenerated d_{xz} and d_{yz} magnetic orbitals of [Co(NC)₂(4-pyridinealdoxime)₄] unit in **3** calculated using DV-X α program.

Table 1

	1	2	3
Formula	C ₁₆ H ₂₀ Mn ₂ N ₁₄ NbO ₅	C ₁₈ H ₂₀ Mn ₂ N ₁₂ NbO ₄	C ₅₆ Co ₂ H ₅₂ N ₂₄ NbO ₁₀
Formula weight	691.21	671.22	1431.94
Crystal system	monoclinic	monoclinic	tetragonal
Space group	<i>P</i> 2 ₁ / <i>n</i> (#14)	<i>P</i> 2 ₁ / <i>n</i> (#14)	<i>I</i> 4 ₁ / <i>a</i> (#88)
<i>a</i> / Å	13.0982(5)	13.1851(3)	20.1981(9)
<i>b</i> / Å	13.2592(5)	13.2870(3)	20.1981(9)
<i>c</i> / Å	15.4421(6)	15.4634(3)	14.9775(6)
β / °	95.997(1)	95.7077(8)	90
<i>V</i> / Å ³	2667.2(2)	2695.6(1)	6110.3(5)
<i>Z</i>	4	4	4
<i>T</i> / K	90(1)	90(1)	293(2)
<i>d</i> _{calc} / g cm ⁻³	1.721	1.654	1.517
<i>F</i> ₀₀₀	1380.00	1340.00	2844.00
Radiation	MoK α (λ = 0.71075 Å)	MoK α (λ = 0.71075 Å)	MoK α (λ = 0.71075 Å)
Data measured	24975	26176	48818
Data unique	6087	6165	3495
<i>R</i> _{int}	0.0447	0.0171	0.1012
GOF	1.113	1.182	1.173
<i>R</i> 1 (<i>I</i> > 2.00 σ (<i>I</i>))	0.0400	0.0218	0.0931
<i>R</i> (all reflections)	0.0453	0.0224	0.1148
<i>wR</i> 2 (all reflections)	0.1099	0.0572	0.2150

Figure 1

(a)

(b)

(c)

(d)

Figure 2

(a)

(b)

(c)

(d)

Figure 3

(a)

(b)

(c)

(d)

Figure 4

Figure 5

(a)

(b)

Figure 6

Figure 7

(a)

(b)

Figure 8

(a)

(b)

(c)

Figure 9

; fUd\ JWU'UVgfrUWh