 

# Cyano-Bridged Gadolinium–Tungstate Bimetallic One-Dimensional Chains with a Dimethylacetamide Ligand

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Reaction of $Gd^{III}(NO)_3 \cdot 6H_2O$ and $(Bu_3NH)_3[W^V(CN)_8]$ ($Bu_3N$ = tributylamine) in *N*,*N*-dimethylacetamide (DMA) yielded two types of Gd–W bimetal assemblies with noncentrosymmetric crystal structures: $Gd^{III}(DMA)_n[W^V(CN)_8]$ ($n = 6$, **1**; $n = 5$, **2**). X-ray single crystal analyses showed that **1** crystallizes in the monoclinic system of the *Cc* space group ($a = 12.6254(6)$ Å, $b = 16.8052(8)$ Å, $c = 20.2499(11)$ Å, $\beta = 103.2893(18)^\circ$, $Z = 4$), and **2** crystallizes in the monoclinic system of the $P2_1$ space group ($a = 9.761(2)$ Å, $b = 19.573(5)$ Å, $c = 10.502(4)$ Å, $\beta = 109.247(12)^\circ$, $Z = 2$). These two crystals consist of one-dimensional linear chains, in which $[Gd^{III}(DMA)_n]^{3+}$ and $[W^V(CN)_8]^{3-}$ ions are linked in an alternating fashion. The difference between these two compounds, that is, **1** contains eight-coordinate $Gd^{III}$ whereas **2** contains seven-coordinate $Gd^{III}$, is due to the temperature during preparation. Magnetic data showed that the magnetic interaction between $Gd^{III}$ ($S = 7/2$) and $W^V$ ($S = 1/2$) is antiferromagnetic coupling of $-0.28(1)\,cm^{-1}$ for **1** and $-0.42(1)\,cm^{-1}$ for **2**.

In the field of molecule-based magnets, cyano-bridged metal assemblies have been aggressively studied to discover novel functionalities.[1] Hexacyanometalate-based materials show interesting functionalities, such as high Curie temperatures,[2] temperature-induced phase transitions,[3] external-stimuli-induced magnetism.[4–9] Recently, octacyanometalate-based magnets have also drawn much attention.[10–21] Octacyanometalates $[M(CN)_8]^{n-}$ (M = Mo, W, etc.) are a versatile class of building blocks that can adopt different spatial configurations, which depend on their chemical environment, e.g., square antiprism ($D_{4d}$), dodecahedron ($D_{2d}$), bicapped trigonal prism ($C_{2v}$). Metal assemblies based on $[M(CN)_8]^{n-}$ can take various coordination geometries in the crystal structure, that is, zero-dimensional (0-D),[11,12] 1-D,[13,14] 2-D,[15–18] and 3-D structures.[19–21] Among these dimensionalities, there are only a few octacyanometalate-based compounds with a 1-D linear chain structure. To date, four compounds, $Gd^{III}(DMF)_6[W^V(CN)_8]$,[14a] $(PPh_4)_2[Ru_2(piv)_4W(CN)_8] \cdot 5H_2O$,[14b] and $Ln^{III}(terpy)(DMF)_4[W^V(CN)_8] \cdot 8H_2O$ (Ln = Gd and Sm),[14c] have been reported. In this work, we prepared two types of octacyanometalate-based compounds with 1-D linear chain structures with electronic polarization, $Gd^{III}(DMA)_6[W^V(CN)_8]$ (**1**) (DMA = dimethylacetamide) and $Gd^{III}(DMA)_5[W^V(CN)_8]$ (**2**), where $Gd^{III}$ and $W^V$ are linked in an alternating fashion. The crystal structures and magnetic properties of these compounds are described in this paper.

## Experimental

**Synthesis. $Gd^{III}(DMA)_6[W^V(CN)_8]$(1):** $(Bu_3NH)_3[W(CN)_8]$ ($Bu_3N$ = tributylamine) of starting material was synthesized according to the method previously described in the literature.[22] A solution of $(Bu_3NH)_3[W(CN)_8]$ ($0.04\,mol\,dm^{-3}$) DMA (2.5 mL) was added, dropwise, to an equimolar solution of $Gd(NO_3)_3 \cdot 6H_2O$ ($0.04\,mol\,dm^{-3}$) DMA (2.5 mL). After slowly diffusing diethyl ether into the mixed solution at 5 °C, pale yellow block crystals were obtained. Yield: 70%. Anal. Calcd $C_{32}H_{54}N_{14}O_6GdW$: C, 35.85; H, 5.08; N, 18.29; Gd, 14.67; W, 17.15%. Found: C, 35.85; H, 5.20; N, 18.58; Gd, 14.81; W, 17.09%. IR: $\nu$(CN) 2127, 2139, 2159, and $2165\,cm^{-1}$.

**$Gd^{III}(DMA)_5[W^V(CN)_8]$ (2):** A solution of $(Bu_3NH)_3[W(CN)_8]$ ($0.04\,mol\,dm^{-3}$) DMA (2.5 mL) was added, dropwise, to an equimolar solution of $Gd(NO_3)_3 \cdot 6H_2O$ ($0.04\,mol\,dm^{-3}$) DMA (2.5 mL). After slowly diffusing diethyl ether into the mixed solution at 30 °C, pale yellow platelet crystals were obtained. Yield: 60%. Anal. Calcd $C_{28}H_{45}N_{13}O_5GdW$: C, 34.15; H, 4.61; N, 18.49; Gd, 15.97; W, 18.67%. Found: C, 34.26; H, 4.74; N, 18.69; Gd, 15.95; W, 18.69%. IR: $\nu$(CN) 2126, 2130, 2135, 2144, and $2171\,cm^{-1}$.

**Measurements.** Elemental analyses of Gd and W for the prepared materials were measured by HP4500 inductively coupled plasma mass spectroscopy (ICP-MS), and those of C, H, and N were determined on a Perkin-Elmer PE2400II CHNS/O. The infrared spectrum was recorded on a Shimadzu FT-IR 8200PC spectrometer with the samples as a paraffin suspension in the 4000–400 $cm^{-1}$ region. Magnetic measurements on a polycrystalline sample were carried out on a Quantum Design MPMS superconducting quantum interference device (SQUID) magnetometer. Pascal's constants were used to determine the diamagnetic contribution.

**Crystallographic Data Collection and Structure Determination.** Table 1 lists the complete crystallographic data and collection parameters for the structures. Single-crystal X-ray data were collected at $90 \pm 1$ K on a Rigaku RAXIS RAPID imaging plate area detector with graphite monochromated Mo K$\alpha$ radiation. The structures were solved by direct methods using SIR2004 for **1** and SIR97 for **2**, which were expanded using Fourier

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Table 1. Crystallographic Data

| | 1 | 2 |
|---|---|---|
| Empirical formula | $C_{32}H_{54}N_{14}O_6GdW$ | $C_{28}H_{45}N_{13}O_5GdW$ |
| $M_r$ | 1071.97 | 984.85 |
| Crystal dimensions/mm$^3$ | 0.17 × 0.17 × 0.10 | 0.30 × 0.17 × 0.08 |
| Crystal system | monoclinic | monoclinic |
| Space group | *Cc* | $P2_1$ |
| $a$/Å | 12.6254(6) | 9.761(2) |
| $b$/Å | 16.8052(8) | 19.573(5) |
| $c$/Å | 20.2499(11) | 10.502(4) |
| $\beta$/° | 103.2893(18) | 109.247(12) |
| $V$/Å$^3$ | 4181.4(4) | 1894.3(9) |
| $d_{calcd}$/g cm$^{-3}$ | 1.703 | 1.727 |
| $T$/K | 90(1) | 90(1) |
| $Z$ | 4 | 2 |
| $\mu$(Mo K$\alpha$)/cm$^{-1}$ | 43.860 | 48.299 |
| Reflections collected | 33473 | 18363 |
| Unique | 9361 ($R_{int}$ = 0.034) | 8101 ($R_{int}$ = 0.029) |
| $R/wR2$ (all data) | 0.028/0.064 | 0.025/0.064 |
| GOF on $F^2$ | 0.991 | 0.993 |
| Flack parameter | 0.008(5) | 0.014(5) |

techniques and refined by full-matrix least-squares techniques using CRYSTALS.[23–25] Some of the DMA molecules were disordered, and atoms in these molecules were refined isotropically. All other non-hydrogen atoms were refined anisotropically. For disordered DMA molecules, the hydrogen atoms could not be located. All other hydrogen atoms were refined using a riding model. The absolute structures were deduced based on the Flack parameter. All calculations were performed using the Crystal Structure crystallographic software package.[26] Table S1 and Table S2 list selected bond distances for **1** and **2**, respectively (Supporting Information).

Crystallographic data have been deposited with Cambridge Crystallographic Data Centre: Deposition number CCDC-656076 for **1**, and CCDC-656077 for **2**. Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

## Results and Discussion

**Crystal Structure.** X-ray single crystal analysis indicates that the crystal structure of **1** is a monoclinic structure in the *Cc* space group ($a$ = 12.6254(6) Å, $b$ = 16.8052(8) Å, $c$ = 20.2499(11) Å, $\beta$ = 103.2893(18)°, $Z$ = 4). Figure 1 shows an asymmetric unit of **1** with the atom-labeling scheme. The asymmetric unit consists of $[Gd^{III}(DMA)_6]^{3+}$ and $[W^V(CN)_8]^{3-}$. The coordination geometry around W is a distorted dodecahedron, in which two CN groups in $[W^V(CN)_8]^{3-}$ are bridged to $Gd^{3+}$ and the other CN groups are free. The W–C bound distances range from 2.16–2.19 Å, and the W–C–N bonds are nearly linear with angles ranging between 177–180°. Gd is coordinated by two cyanonitrogens (N3a and N8) [symmetry operation: (a) $x$, $-y+2$, $z-1/2$] and six oxygen atoms from DMA molecules. The coordination geometry around Gd is bicapped trigonal prism, in which the Gd–N distances range from 2.59–2.63 Å and the Gd–O distances range from 2.31–2.43 Å. The Gd–N–C bonds are slightly bent with angles ranging between 170–175°. Figure 2 shows a packing

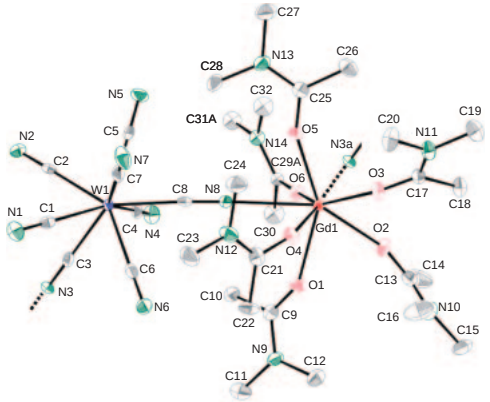



Fig. 1. Thermal ellipsoid plot showing the asymmetric unit and atom numbering scheme of **1**. Displacement ellipsoids are drawn at a 50% probability level. Hydrogen atoms are omitted for clarity [Symmetry codes: (a) $x$, $-y+2$, $z-1/2$].

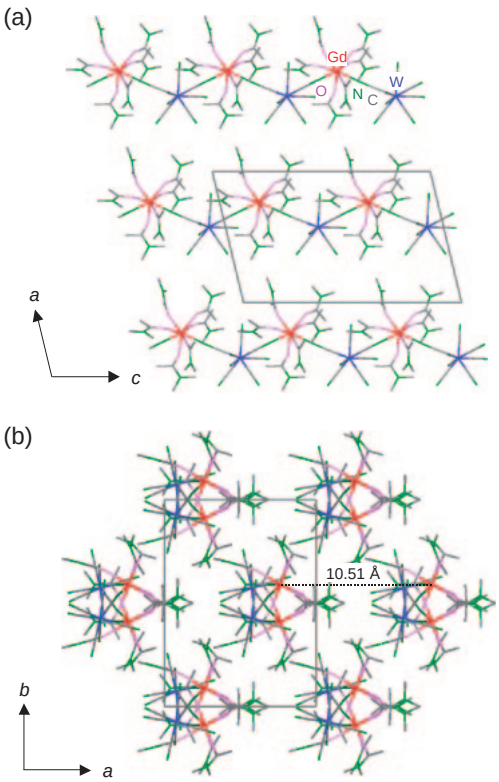



Fig. 2. Views of the crystal structure of **1**. Blue, red, gray, green, and pink represent W, Gd, C, N, and O, respectively. (a) The projection in the *ac* plane. (b) The projection in the *ab* plane. Hydrogen atoms are omitted for clarity.

diagram for **1**. $[Gd^{III}(DMA)_6]^{3+}$ and $[W^V(CN)_8]^{3-}$ are linked in an alternating fashion to form a 1-D cyano-bridged chain. Each unit cell has two equivalent chains. Each chain grows in the crystallographic $c$ direction and is separated from the nearest chains with the shortest intermetallic distance between Gd and Gd (equal to the one between W and W) of 10.51 Å. This compound has a pyroelectric crystal structure, in which the electric polarization is along $a$ axis.

Next, we examined the crystal structure of **2**. X-ray single

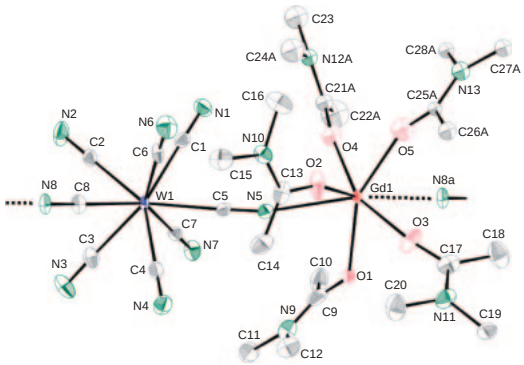



Fig. 3. Thermal ellipsoid plot showing the asymmetric unit and atom numbering scheme of **2**. Displacement ellipsoids are drawn at a 50% probability level. Hydrogen atoms are omitted for clarity [Symmetry codes: (a) $x, y, z-1$].

crystal analysis shows that **2** crystallizes in the monoclinic space group $P2_1$ ($a = 9.761(2)$ Å, $b = 19.573(5)$ Å, $c = 10.502(4)$ Å, $\beta = 109.247(12)^\circ$, $Z = 2$). The asymmetric unit consists of $[Gd^{III}(DMA)_5]^{3+}$ and $[W^V(CN)_8]^{3-}$, as shown in Fig. 3. The coordination geometry around W is dodecahedron. Two CN groups in $[W^V(CN)_8]^{3-}$ are bridged to $Gd^{3+}$, and the other CN groups are free. The W–C bound distances range from 2.15–2.19 Å, and the W–C–N bonds are nearly linear with angles ranging between 178–179°. Gd is coordinated by two cyanonitrogens (N5 and N8a) [symmetry operation: (a) $x, y, z-1$] and five oxygen atoms from DMA molecules. The coordination geometry around Gd is a distorted capped octahedron, in which the Gd–N distances range from 2.50–2.51 Å and Gd–O distances range from 2.26–2.31 Å. The Gd–N–C bonds are slightly bent with angles ranging between 169–176°. Figure 4 shows a packing diagram of **2**. $[Gd^{III}(DMA)_5]^{3+}$ and $[W^V(CN)_8]^{3-}$ are linked in an alternating fashion to form a 1-D cyano-bridged chain. Each unit cell has two equivalent chains in which each chain grows in the crystallographic *c* direction. The shortest intermetallic distance between one chain and the nearest chains (Gd and Gd, or W and W) is 9.76 Å. **2** also has a pyroelectric crystal structure, in which the electric polarization is along the *b* axis.

The mechanism for the reaction temperature dependence on the crystal structure is considered as follows. It has been reported that, in the solvation effect of DMA molecule, the solvation number of DMA to 3d metal ions decreases as the temperature increases due to the steric effect of bulky DMA molecules.[27] The dependence of the ionic size of lanthanide ions in the DMA solvation effect has also been reported and indicates that the solvation number is eight for $La^{3+}$ (1.18 Å) and seven for $Lu^{3+}$ (0.97 Å) in DMA and that an equilibrium between eight- and seven-coordination is established for intermediate rare earth metal ions.[28]

Based on these reports, Scheme 1 depicts the equilibrium between eight- and seven-coordination for $Gd^{3+}$ in DMA solution, where an increase in temperature ($5 \rightarrow 30\,^\circ$C) shifts this equilibrium to right side. When $[W^V(CN)_8]^{3-}$ reacts with $[Gd^{III}(DMA)_8]^{3+}$ and two DMA molecules are subsequently eliminated, **1**, which contains eight-coordinated $Gd^{III}$, is obtained. In contrast, when $[W^V(CN)_8]^{3-}$ reacts with $[Gd^{III}(DMA)_7]^{3+}$ and two DMA molecules are subsequently eliminated, **2**, which contains seven-coordinated $Gd^{III}$, is obtained.

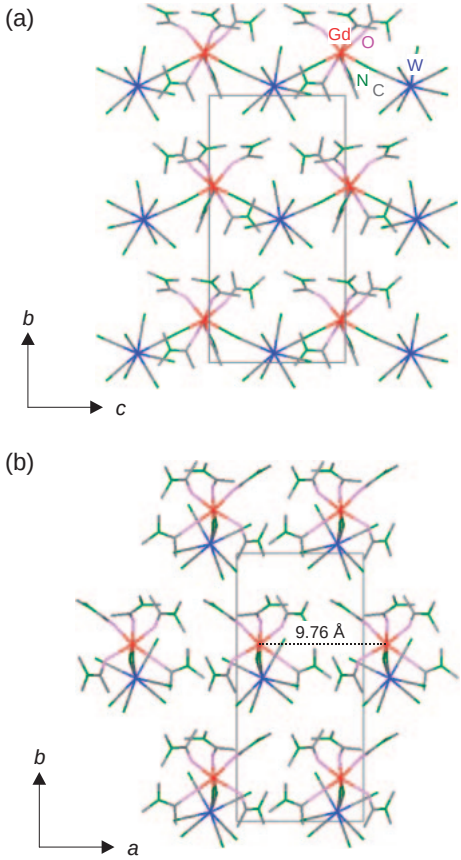
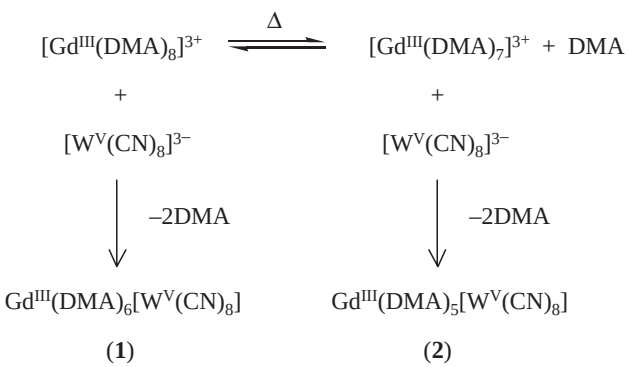



Fig. 4. Views of the crystal structure of **2**. Blue, red, gray, green, and pink represent W, Gd, C, N, and O, respectively. (a) The projection in the *bc* plane. (b) The projection in the *ab* plane. Hydrogen atoms are omitted for clarity.




Scheme 1.

**Magnetic Properties.** The temperature dependence of the magnetic susceptibility ($\chi_M$) was recorded with an applied field of 1 kOe in the temperature range of 1.8–300 K at a rate of 1 K min$^{-1}$. Figure 5a shows the temperature dependence of the product of $\chi_M$ and the temperature ($T$) for **1**. The $\chi_M T$ value at 300 K was 8.2 K cm$^3$ mol$^{-1}$, which is close to the expected spin-only value of 8.3 K cm$^3$ mol$^{-1}$ for one $Gd^{III}$ ($S_{Gd} = 7/2$) and one $W^V$ ($S_W = 1/2$), assuming a $g$ value of 2.0. The $\chi_M T$ value gradually decreased as $T$ decreased and reached a minimum value of 7.5 K cm$^3$ mol$^{-1}$ at 3.4 K; however, it then increased to 7.8 K cm$^3$ mol$^{-1}$ at 1.8 K. In the

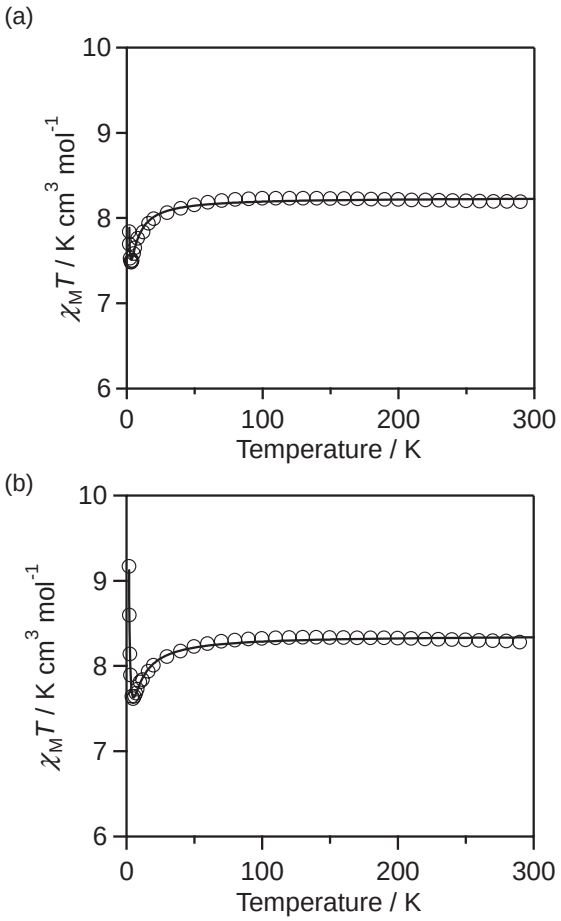



Fig. 5. $\chi_M T$–$T$ plots under an applied field of 1000 G of (a) **1** and (b) **2**. Solid lines represent the fitted line by Seiden's model.

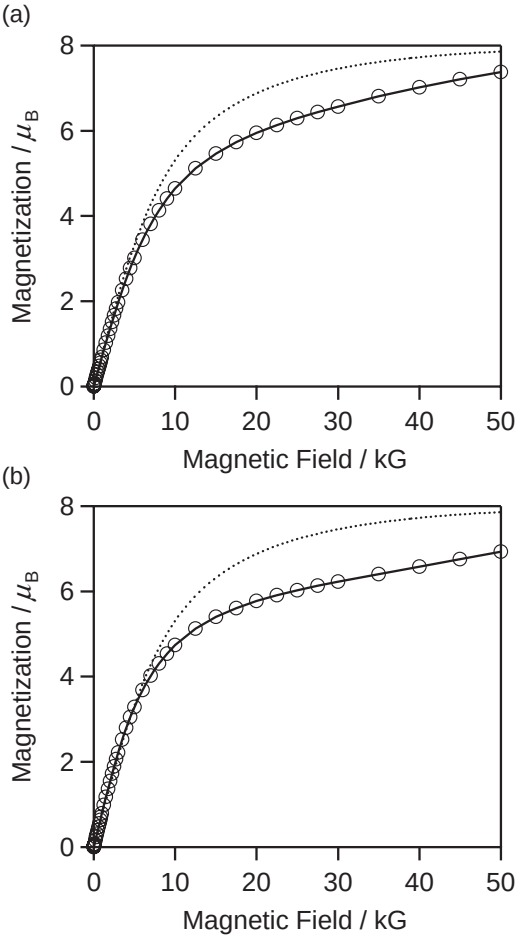



Fig. 6. Magnetization vs. external magnetic field plots at 2 K for (a) **1** and (b) **2**. The dotted line represents the sum of the Brillouin functions of $S = 7/2$ and $S = 1/2$.

$\chi_M T$–$T$ plots for **2** (Fig. 5b), the $\chi_M T$ value at 300 K is 8.3 K cm$^3$ mol$^{-1}$, which is consistent with the expected spin-only value of 8.3 K cm$^3$ mol$^{-1}$ for one Gd$^{III}$ ($S_{Gd} = 7/2$) and one W$^V$ ($S_W = 1/2$), assuming a $g$ value of 2.0. The $\chi_M T$ value gradually decreased as $T$ decreased, and reached a minimum value (7.8 K cm$^3$ mol$^{-1}$) at 4.8 K, and then increased to 9.2 K cm$^3$ mol$^{-1}$ at 1.8 K. In the magnetization vs. external magnetic field plots at 2 K (Fig. 6), the magnetization reached 7.4 $\mu_B$ for **1** and 6.9 $\mu_B$ for **2**. In the temperature dependence of in-phase components ($\chi_M'$) of the ac magnetic susceptibility, $\chi_M'$ increased monotonically as temperature decreased, whereas no signal was observed in out-of-phase components ($\chi_M''$). Both components showed no frequency dependence in the frequency range between 0.1 and 1000 Hz (Supporting Information).

The $\chi_M T$–$T$ plots were analyzed based on a model that assumes an alternate arrangement of classical spins ($S^A$) and quantum spins ($S^B$), i.e., $\cdots - S^A{}_{2i-1} - S^B{}_{2i} - S^A{}_{2i+1} - \cdots$ (Seiden's model).[29] In this model, the spin Hamiltonian ($\hat{H}$) with an exchange interaction ($J$) is defined as $\hat{H} = -2J\Sigma(S^A{}_{2i-1} + S^A{}_{2i+1})S^B{}_{2i}$, where $S^A{}_{2i\pm1}$ and $S^B{}_{2i}$ refer to $S_{Gd}$ and $S_W$, respectively. Assuming $g_{Gd}$ and $g_W$ values of 2.0, the value of $J$ was fitted to the experimental data in the temperature range 1.8–300 K with $J = -0.28(1)$ cm$^{-1}$ for **1** as shown by the solid line in Fig. 5a. This negative $J$ value indicates an antiferromagnetic interaction between Gd$^{III}$ and W$^V$, and that the present compound is a ferrimagnetic 1-D chain. Deviation from the $M$–$H$ curve due to the sum of the Brillouin functions, $B_S$, for Gd$^{III}$ ($S = 7/2$) and W$^V$ ($S = 1/2$) also supports the presence of the antiferromagnetic interaction between these two magnetic ions. The $\chi_M T$–$T$ plot for **2** was fitted with $J = -0.42(1)$ cm$^{-1}$, indicating compound **2** is also a ferrimagnetic 1-D chain.

Table 2 lists the exchange interaction, coordination geometry around W$^V$, intra-chain distance between W$^V$ and Gd$^{III}$, and minimum intermetallic distance between one chain and the nearest chains of the previously reported and the present one-dimensional compounds. In all of the compounds, the magnetic interaction between Gd$^{III}$ and W$^V$ is antiferromagnetic. Both DMA compounds show smaller $|J|$ values than the other two. Focusing on the coordination geometry around W$^V$, both Gd(DMF)$_6$[W(CN)$_8$] and [Gd(terpy)(DMF)$_4$][W(CN)$_8$]·8H$_2$O are square antiprisms, whereas the both present compounds are dodecahedrons. In dodecahedral geometry, the eight vertexes are geometrically unequal, and they can be classified as $\alpha$ and $\beta$ sites as shown Fig. 7a. On the other hand, the eight vertexes are geometrically equal with a square antiprismatic geometry as shown Fig. 7b ($\gamma$ site). Thus, to discuss a geometrical effect on the superexchange interaction, we investi-

Table 2. Structural Parameter and Exchange Interaction of $Gd^{III}$–$[W^{V}(CN)_8]$ 1-D Linear Chain Compounds

| | $Gd(DMF)_6[W(CN)_8]$ | $[Gd(terpy)(DMF)_4][W(CN)_8]\cdot 8H_2O$ | **1** | **2** |
|---|---|---|---|---|
| Exchange interaction $J/cm^{-1}$ | −0.58 | −0.8 | −0.28 | −0.42 |
| Coordination geometry around W[a)] | SAP | SAP | DD | DD |
| Intra-chain distances between $Gd^{III}$–$W^{V}$/Å | 5.84<br>5.81 | 5.82<br>5.88 | 5.89<br>5.97 | 5.80<br>5.81 |
| Inter-chain distances/Å | 8.60 | 9.1 | 10.51 | 9.761 |
| Reference[b)] | 14a | 14c | | |

a) SAP = square antiprism, DD = dodecahedron. b) Ref. 14a: S. Ikeda, T. Hozumi, K. Hashimoto, S. Ohkoshi, *Dalton Trans.* **2005**, 2120. Ref. 14c: P. Przychodzeń, K. Lewiński, R. Pełka, M. Bałanda, K. Tomala, B. Sieklucka, *Dalton Trans.* **2006**, 625.

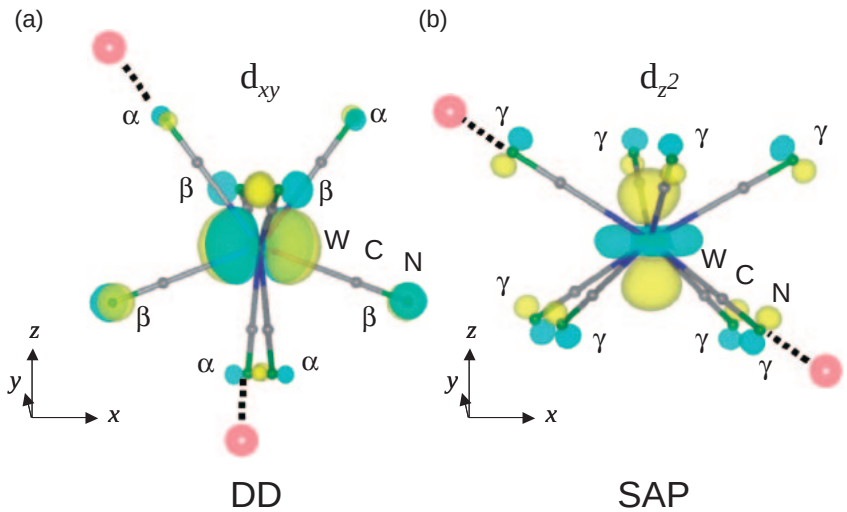



Fig. 7. Magnetic orbital of $[W^{V}(CN)_8]^{3-}$ calculated by DV-X$\alpha$ method: (a) dodecahedron (Dashed lines indicate bridging CN groups in **1** and **2**.), (b) square antiprism (Dashed lines indicate bridging CN groups in $Gd(DMF)_6[W(CN)_8]$ and $[Gd(terpy)(DMF)_4][W(CN)_8]\cdot 8H_2O$.).

gated the magnetic orbital of $[W^{V}(CN)_8]^{3-}$ with idealized dodecahedral (DD) and square antiprismatic (SAP) geometries[30] by DV-X$\alpha$ molecular orbital calculations.[31] Figure 7 shows the calculated magnetic orbitals. Both geometries possess a nondegenerate d orbital with an unpaired electron. This orbital is the $d_{xy}$ for the DD[32] and the $d_{z^2}$ for the SAP. In the DD, there is a difference in the contribution of the p orbital on the N atoms to the magnetic orbital between the $\alpha$ site and $\beta$ site, whereas that in the SAP is the same among all $\gamma$ sites. Recently, Sutter et al.[33] have suggested a relation using density-functional theory calculation. Their calculation demonstrates that the spin density on cyanonitrogen in the SAP $\gamma$ site (SAP-$\gamma$) is larger than that on DD $\alpha$ site (DD-$\alpha$), but smaller than that on DD $\beta$ site (DD-$\beta$), i.e., $|J_{DD\text{-}\alpha}| < |J_{SAP\text{-}\gamma}| < |J_{DD\text{-}\beta}|$. In both compounds **1** and **2**, all of the bridging sites are DD $\alpha$ sites (Supporting Information). Therefore, their $|J|$ values are smaller than that of the other two compounds, whose bridging sites are SAP $\gamma$ sites.

## Conclusion

We prepared new $Gd^{III}$–$W^{V}$ bimetallic assemblies with 1-D linear chain structures, $Gd(DMA)_6[W(CN)_8]$ and $Gd(DMA)_5[W(CN)_8]$. The difference between the two structures is the number of DMA molecules that coordinate to $Gd^{III}$, which is controlled by reaction temperature. Both compounds have noncentrosymmetric structures with electronic polarizations. These compounds are the first examples of pyroelectric crystals based on 1-D octacyanometalate chain. Analyses using Seiden's model showed that an antiferromagnetic superexchange interaction with $J$ values of $-0.28(1)\,cm^{-1}$ for **1** and $-0.42(1)\,cm^{-1}$ for **2** operates between $Gd^{III}$ and $W^{V}$ through the CN bridges.

Recently, magnetic complexes with low-dimensional structure have attracted attention. Because cyano-bridged metal assemblies containing lanthanide ions often show low-dimensional structure,[34,35] lanthanide ions should also effectively form low-dimensional octacyanometalate-based metal assemblies. In addition, because rare-earth metals can cause various magnetic anisotropies due to their orbital angular momentum, interesting magnetic properties are expected.[16b,36] Hence, we are currently synthesizing octacyanometalate-based complexes of other lanthanide ions with the DMA ligand to add a large magnetic anisotropy to our 1-D materials.

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## Supporting Information

Selected bond length and angles for **1** and **2**, temperature dependence of ac magnetic susceptibility for **1** and **2**, and Magnetic orbital of $[W^{V}(CN)_8]^{3-}$ calculated by DV-X$\alpha$ method for **1** and **2**. This material is available free of charge on the web at http://www.csj.jp/jounals/bcsj/.

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