Network dimensionalities and thermal expansion properties of metal nitroprussides

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Network dimensionalities and thermal expansion properties of metal nitroprussides

Tomoyuki Matsuda,‡ Jungeun Kim and Yutaka Moritomo*‡

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We investigated the thermal expansion properties of metal nitroprussides, \(M_A[Fe(CN)_5NO] \cdot zH_2O\) (\(M_A = \) Mn, Fe, Co, Ni, Cu, Zn, and Cd), which have various network structures, i.e. three-dimensional (3D) cubic (\(Fm\overline{3}m\) for \(M_A = \) Fe, Co, and Ni), distorted three-dimensional (distorted-3D) orthorhombic (\(Pnma\) for \(M_A = \) Mn, Zn, and Cd), and two-dimensional (2D) orthorhombic (\(Am\overline{2}m\) for \(M_A = \) Cu) structures. In the cubic system, in which the unbridged NO groups are randomly distributed, isotropic positive thermal expansion was observed. On the contrary, in the orthorhombic system, in which the unbridged NO groups are uniaxially distributed, positive (negative) thermal expansion was observed along (perpendicular to) the uniaxial direction. We interpreted the characteristic thermal responses in terms of the rotational vibrations of the \([Fe(CN)_5NO]\) units as well as their steric hindrances due to the network dimensionalities.

In this work, we systematically studied the thermal expansion properties of metal nitroprussides, \(M_A[Fe(CN)_5NO] \cdot zH_2O\) (\(M_A = \) Mn, Fe, Co, Ni, Cu, Zn, and Cd), in which one of the CN groups are replaced by the NO group. The unbridged NO group modified the dimensionality of the cyano-bridged network structure. Based on the structural analysis, we classified the network structure into three categories, i.e., 3D cubic (\(Fm\overline{3}m\) for \(M_A = \) Fe, Co, and Ni), distorted three-dimensional (distorted-3D) orthorhombic (\(Pnma\) for \(M_A = \) Mn, Zn, and Cd), and two-dimensional (2D) orthorhombic (\(Am\overline{2}m\) for \(M_A = \) Cu) structures. We found that the variation of the network dimensionality crucially influence the thermal expansion properties. We interpreted the dimensionality-dependence of the thermal expansion in terms of the rotational vibrations of the \([Fe(CN)_5NO]\) units as well as their steric hindrances.

Introduction
Thermal expansion properties in network structures are attracting a considerable interest of the materials scientists, due to the possibility of zero/negative thermal expansion properties.1 Recently, coordination polymer frameworks are found to show negative thermal expansion (NTE) behaviors.2–6 The NTE behaviors in such framework systems are generally attributed to the flexibility of the structure, in which thermal population of low-energy transverse and/or rotational vibrations of the molecular units. Such a flexibility of the lattice causes interesting physical properties, such as pressure-induced structural phase transition,7 pressure-induced amorphization,8 and large Grüneisen parameter.9 In addition, materials with NTE behaviors are useful in variety of electronics application and as components of high-precision thermometers.

Prussian blue type cyanides, \(A_M[A[Fe(CN)_5]_6] \cdot zH_2O\) (\(A = \) alkali metal ion, \(M_A = Mn, Fe, Co, Ni, Cu, Zn and Cd, and \(M_B = Fe, Co, Pt\) shows characteristic thermal expansion properties.3–6 The compounds belong to face-centered cubic (\(Fm\overline{3}m\); \(Z = 4\)) structures, in which \(M_A\) and \(M_B\) are bridged by the cyano groups and form a three-dimensional (3D) network structure.10 The alkali metal cations and water molecules are accommodated in the interstitial sites of the lattice. The thermal expansion coefficient \((\beta = d\alpha/dT)\) of the lattice constant \(\alpha\) systematically decreases with an increase in \(\alpha\): \(\beta = +1.49 \times 10^{-5} \text{K}^{-1}\) for \(Rb_{0.39}Co[Fe(CN)_5]_{1.10} \cdot 3.8H_2O\) \((\alpha = 9.943 \text{ Å})\) and \(\beta = -0.88 \times 10^{-5} \text{K}^{-1}\) for \(Cs_{1.00}Cd[Fe(CN)_5]_{1.00} \cdot 0.5H_2O\) \((\alpha = 10.755 \text{ Å})\). The systematic change in \(\beta\) is well explained by the thermally-induced rotational vibrations of the \([Fe(CN)_5]_6\) units as well as their steric hindrances. According to this scenario, we may significantly control the thermal expansion properties by the modification of the dimensionality of the cyano-bridged network.

Experimental
Powders of \(M_A[Fe(CN)_5NO] \cdot zH_2O\) \((M_A = Fe, Co, Ni, Cu, Zn, and Cd)\) were prepared by reacting an aqueous solutions of \(MnCl_2\cdot 4H_2O\), \(FeCl_2\cdot 4H_2O\), \(CoCl_2\cdot 6H_2O\), \(NiCl_2\cdot 6H_2O\), \(CuCl_2\cdot 2H_2O\), \(ZnCl_2\), \(CdCl_2\cdot 2.5H_2O\), and \(Na_2[Fe(CN)_3NO] \cdot 2H_2O\). The precipitated powders were filtered and washed with water and then dried in air. Chemical compositions of the prepared samples were determined by inductively coupled plasma atomic emission spectrometry (ICP-AES) for metal elements and standard microanalytical methods for C, H, and N elements. Elemental analyses showed that the formulas of the obtained compounds were \(Mn[Fe(CN)_5NO] \cdot 2H_2O\) \((Mn)\), \(Fe[Fe(CN)_5NO] \cdot 5.0H_2O\) \((Fe)\), \(Co[Fe(CN)_5NO] \cdot 5.4H_2O\) \((Co)\), \(Ni[Fe(CN)_5NO] \cdot 5.8H_2O\) \((Ni)\), \(Cu[Fe(CN)_5NO] \cdot 2.2H_2O\) \((Cu)\), \(Zn[Fe(CN)_5NO] \cdot 2.0H_2O\) \((Zn)\), \(Cd[Fe(CN)_5NO] \cdot 2.3H_2O\) \((Cd)\), respectively: calculated wt% for \(Mn: Mn, 17.80; Fe, 18.09; C, 19.45; N, 27.22; H, 1.37\%: found; Mn, 17.55; Fe, 18.10; C,
19.48; N, 27.18; H, 1.31%; calculated wt% for Fe, 30.86; C, 16.60; N, 23.23; H, 2.79%; found; Fe, 30.43; C, 16.71; N, 23.17; H, 1.985%; calculated wt% for Co, 15.84; Fe, 15.01; C, 16.14; N, 22.58; H, 2.92%; found; Co, 15.72; Fe, 15.02; C, 16.34; N, 22.34; H, 2.68%; calculated wt% for Ni, 15.17; Fe, 14.86; C, 15.98; N, 22.37; H, 3.02%; found; Ni, 15.24; Fe, 14.85; C, 16.02; N, 22.23; H, 2.86%; calculated wt% for Cu, 19.91; Fe, 17.50; C, 18.82; N, 26.34; H, 1.39%; found; Cu, 19.77; Fe, 17.78; C, 18.97; N, 26.32; H, 1.21%; calculated wt% for Zn, 20.60; Fe, 17.60; C, 18.92; N, 26.48; H, 1.27%; found; Zn, 20.08; Fe, 17.46; C, 19.01; N, 26.46; H, 0.90%; calculated wt% for Cd, 30.40; Fe, 15.10; C, 16.24; N, 22.73; H, 1.25%; found; Cd, 30.22; Fe, 15.27; C, 16.54; N, 22.62; H, 0.81%.

In order to precisely determine a and the space groups of the above-synthesized metal nitroprussides, X-ray powder-diffraction patterns were measured at the synchrotron-radiation facility, SPring-8. First, powder samples were filled into 0.3 mm θ glass capillary. The capillary was put on a Debye-Scherrer camera at the BL02B2 beamline of SPring-8.11 The wavelength of the X-ray (λ ~ 0.5 Å) was calibrated by the lattice constant of standard CeO2 powder. The sample temperature was controlled by the cooled nitrogen gas. The exposure time was 5 min. The lattice constants of each compound were refined by the RIETAN-FP program,12 and the 2θ range used in the Rietveld analyses were 3°~30°.

### Results and discussion

#### Materials

The metal nitroprussides are known to show several types of crystal structures.13-30 We performed Rietveld analysis of the synchrotron-radiation X-ray powder diffraction patterns of the obtained compounds, and found that the compounds are classified into three types of crystal structures according to the metal ion (Table 1). We show in Fig. 1 the prototypical diffraction patterns at 300 K together with the results of Rietveld refinements. In the inset of Fig. 1, we depicted schematic crystal structures.

The cubic compounds (Fe, Co, and Ni) show 3D network structures similar to the case of the Prussian blue analogues. Here, we note that the five cyano groups of [Fe(CN)5NO] are bridged to the neighboring M while the NO group is unbridged.35

On the contrary, the orthorhombic compounds (Mn, Cu, Zn, and Cd) have rather complicated network structures (Fig. 2). The Mn, Zn, and Cd compounds show distorted-3D network structure. Within the ab plane (Fig. 2a, left), MA atoms are surrounded by four cyanide nitrogen atoms of [Fe(CN)5NO] forming cyano-bridged 2D layers (M—N—C—Fe). Along the c axis (Fig. 2a, right), one side of MA is coordinated to cyanide nitrogen atom of [Fe(CN)5NO], while the other side is coordinated to the oxygen atom of the water ligand. That is, the five cyano groups of [Fe(CN)5NO] are bridged to the neighboring MA while the NO group is unbridged. Due to the steric confinement between the free NO group of [Fe(CN)5NO], and water ligand of MA, the cyano-bridged MA-Fe layers along the ab plane are significantly distorted. The Cu compound shows 2D network structure. Within the ab plane (Fig. 2a, left), Cu atoms are surrounded by four cyanide nitrogen atoms of [Fe(CN)5NO]. Along the c axis (Fig. 2a, right), however, both sides of Cu atoms are coordinated to the oxygen atoms of water ligands. That is, the four CN groups of [Fe(CN)5NO] are bridged to the neighboring Cu in the ab plane while the remaining CN group and the NO group are unbridged along the c axis. The cyano-bridged Cu-Fe layers stack alternately along the c axis, causing 2D network structure.

#### Table 1 Chemical composition, space group, lattice constant at 100 K for M₅[Fe(CN)₅NO]·zH₂O.

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<tr>
<td>Mn[Fe(CN)₅NO]·2H₂O</td>
<td>Pnma</td>
</tr>
<tr>
<td>Fe[Fe(CN)₅NO]·5H₂O</td>
<td>Fm3m</td>
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<tr>
<td>Co[Fe(CN)₅NO]·5H₂O</td>
<td>Fm3m</td>
</tr>
<tr>
<td>Ni[Fe(CN)₅NO]·5H₂O</td>
<td>Fm3m</td>
</tr>
<tr>
<td>Cu[Fe(CN)₅NO]·2.2H₂O</td>
<td>Amm2</td>
</tr>
<tr>
<td>Zn[Fe(CN)₅NO]·2.0H₂O</td>
<td>Pnma</td>
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<tr>
<td>Cd[Fe(CN)₅NO]·2.3H₂O</td>
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The 422 reflection shifts to the high-angle side with decrease in temperature. The reliable factor $R_b$ ranges from 1.01 to 2.80%. To evaluate the thermal expansion of cyano-bridged ab plane, we use the geometrical average of the lattice constants ($a' = a^{1/2} \times b^{1/2}$). We show the temperature dependences of $a'$ and $c$ values in Fig. 4. We determined $\beta$ by the least-squares fittings. The $\beta$ values are $-9.8 \times 10^{-7} / K (a')$, and $5.35 \times 10^{-5} / K (c)$ for Mn, $-4.3 \times 10^{-6} / K (a')$, and $5.19 \times 10^{-5} / K (c)$ for Zn, and $-3.4 \times 10^{-6} / K (a')$, and $6.63 \times 10^{-5} / K (c)$ for Cd.

![Fig. 1](image1.png)

**Fig. 1** X-ray powder diffraction patterns at 100 K and Rietveld analysis of Co (a), Mn (b), and Cu (c). Red dots, black line, and blue line are the observed plots, calculated pattern, and their difference, respectively. Green bars represent the calculated positions of the Bragg reflections.

We show typical examples of the magnified X-ray diffraction patterns around 200, 020, 004, and 220 reflections in Cu, which have 2D network structure. The 020 and 004 reflections shift to the high-angle side with decrease in temperature, reflecting PTE along b axis. The lattice constants are refined against temperature. The reliable factor $R_b$ ranges from 2.64 to 6.28%. The temperature dependences of the normalized lattice constants are plotted in Fig. 3. We determined $\beta$ by the least-squares fittings; $\beta = 8.5 \times 10^{-6} / K (Fe), 6.9 \times 10^{-6} / K (Co)$, and $7.0 \times 10^{-6} / K (Ni)$.

![Fig. 2](image2.png)

**Fig. 2** Schematic crystal structures of distorted-3D network for Mn, Zn, and Cd (a), and 2D network for Cu (b). (left) The projection in the ab plane. (right) Network structure perpendicular to the ab plane.

**Thermal expansion properties**

We show typical examples of the magnified X-ray diffraction patterns around 422 reflection in Fe, Co, and Ni in Fig. S1 (ESI). The 422 reflection shifts to the high-angle side with decrease in temperature, reflecting PTE. The lattice constants were refined against temperature. The reliable factor $R_b$ ranges from 2.64 to 6.28%. The temperature dependences of the normalized lattice constants are plotted in Fig. 3. We determined $\beta$ by the least-squares fittings; $\beta = 8.5 \times 10^{-6} / K (Fe), 6.9 \times 10^{-6} / K (Co)$, and $7.0 \times 10^{-6} / K (Ni)$.

![Fig. 3](image3.png)

**Fig. 3** Temperature dependences of the normalized lattice constants for Fe (a), Co (b), and Ni (c). The lines are the results of the least-squares fittings.

Next, we show in Fig. S2 (ESI) typical examples of the magnified X-ray diffraction patterns around 020, 311, and 212 reflections in Mn, Zn, and Cd, which have distorted-3D networks. The 311 and 212 reflection shift to the high-angle side with decrease in temperature, reflecting positive thermal expansion (PTE). On the contrary, 020 reflection shifts to the low-angle side with decrease in temperature, reflecting NTE along b axis. The lattice constants are refined against temperature. The reliable factor $R_b$ ranges from 3.08 to 2.80%. To evaluate the thermal expansion of cyano-bridged ab plane, we use the geometrical average of the lattice constants ($a' = a^{1/2} \times b^{1/2}$). We show the temperature dependences of $a'$ and $c$ values in Fig. 4. We determined $\beta$ by the least-squares fittings. The $\beta$ values are $-9.8 \times 10^{-7} / K (a')$, and $5.35 \times 10^{-5} / K (c)$ for Mn, $-4.3 \times 10^{-6} / K (a')$, and $5.19 \times 10^{-5} / K (c)$ for Zn, and $-3.4 \times 10^{-6} / K (a')$, and $6.63 \times 10^{-5} / K (c)$ for Cd.

![Fig. 4](image4.png)

**Fig. 4** Temperature dependences of the normalized $a' (= a^{1/2} \times b^{1/2})$ and $c$ for Mn (a), Zn (b), and Cd(c). The lines are the results of the least-squares fittings.

We show in Fig. S3 (ESI) typical example of magnified X-ray diffraction patterns around 200, 020, 004, and 220 reflections in Cu, which have 2D network structure. The 020 and 004 reflection shift to the high-angle side with decrease in temperature, reflecting PTE along b and c axes. On the contrary, 200 and 220 reflections shift to the low-angle side with decrease in temperature, reflecting NTE along a axis and ab plane. The lattice constants of Cu are refined against temperature, and the reliable factor $R_b$ ranges from 3.08 to 3.41%. To evaluate the thermal expansion of cyano-bridged ab plane, we use the geometrical average of the lattice constants ($a' = a^{1/2} \times b^{1/2}$). We show in Fig. 5 the normalized values of $a'$ and $c$ against temperature. We determined $\beta$ by the least-squares fitting, and the $\beta$ values are $-5.2 \times 10^{-6} / K (a')$, and $1.20 \times 10^{-4} / K (c)$

![Fig. 5](image5.png)

**Fig. 5** Temperature dependence of the normalized $a' (= a^{1/2} \times b^{1/2})$ and $c$ for Cu. The lines are the results of the least-squares fittings.

**Relation between network dimensionalities and thermal expansion behaviors**

Here, we discuss the relation between thermal expansion behavior and dimensionality. We plot the in-plane and out-of-plane components of the thermal expansion against $M_a$ for
$M_4[\text{Fe(CN)}_5\text{NO}]\cdot\text{H}_2\text{O}$. The Fe, Co, and Ni compounds show 3D network, the Mn, Zn, and Cd compounds show distorted-3D network, and the Cu compounds shows 2D network.

In the in-plane components (Fig. 6a), the distorted-3D and 2D systems show NTE, while the 3D system shows PTE. This dimensionality dependences of the thermal expansion is well understood by the steric hindrance effect. The origin of the NTE can be ascribed to the rotational vibrations of the $[\text{Fe(CN)}_5\text{NO}]$ units, analogous to the case of the Prussian blue analogues. In the distorted-3D and 2D systems, there exist enough spaces for the $[\text{Fe(CN)}_5\text{NO}]$ units to show thermally-induced rotational vibrations (Fig. 2). Then, the rotational vibration causes the NTE observed. In the 3D system, however, the steric hindrances suppress the rotational vibration. Then, the inherent PTE overcomes the NTE behavior.

In the out-of-plane components (Fig. 6b), the magnitude of PTE increases with decrease in the dimensionality. This is because the chemical bonds between the cyano-bridged layers become weaker as the dimensionality decreases. Actually, the number $N$ of the cyano-bridge per one $[\text{Fe(CN)}_5\text{NO}]$ between the layers decrease from 1.67 ($= 2 \times (5/6)$) for the 3D system, 1 for the distorted-3D system, and 0 for the 2D system. The reduction of the cyano-bridge weakens the inter-layer interaction, and enhances the PTE behavior.

**Fig. 6** (a) In-plane, and (b) out-of-plane components of the thermal expansion against $M_4$ for $M_4[\text{Fe(CN)}_5\text{NO}]\cdot\text{H}_2\text{O}$. The Fe, Co, and Ni compounds with 3D network (closed squares), the Mn, Zn, and Cd compounds with distorted-3D network (closed diamonds), and the Cu compound with 2D network (closed circles).

**Conclusions**

In conclusion, we demonstrated that the anisotropic thermal expansion properties of the metal nitroprussides significantly depend on the dimensionality of the network structure. The dimensionality dependence of the thermal expansion is well explained by the rotational vibrations of $[\text{Fe(CN)}_5\text{NO}]$ units as well as their steric hindrances. Here, we emphasize that the metal nitroprussides is a unique system, in which the dimensionality of the cyano-bridged transition metal network can be controlled by chemical substitution of the $M_4$ site.

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**Notes and references**

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