

A Novel Cyanide-Bridged Thulium-Nickel Heterobimetallic Polymeric Complex $\{(H_2O)_2(DMF)_{10}Tm_2[Ni(CN)_4]_2\}[Ni(CN)_4]$ including O-H \cdots N Hydrogen Bond

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The synthetic procedure for the preparation of heterobimetallic complexes containing lanthanide and transition metals have been intensively developed because they can be used in catalysis^{1,2} and material applications.³ Direct metal bonds between transition metals and lanthanide metals are relatively rare⁴ and the heterobimetallic complexes with bridging ligands should be more accessible. The cyanide groups of $[M(CN)_4]^{2-}$ (M = transition metal) can be used as bidentate ligands which bridge metal atoms.^{5,6} Therefore, our focus has been on synthesizing the lanthanide and transition heterobimetallic complexes containing cyanide-bridged ligands. We have investigated the preparation of cyanide-bridged lanthanide and transition heterobimetallic complexes.⁷ Recently, we have been interested in the heterobimetallic complexes including coordinated water molecules, because there are significant differences in physical properties and coordination geometries between water-free complexes and those.⁸

Here we describe detail of the synthesis and crystal structure of a novel cyanide-bridged thulium(III) nickel heterobimetallic polymeric complex $\{(H_2O)_2(DMF)_{10}Tm_2[Ni(CN)_4]_2\}[Ni(CN)_4]$ prepared quantitatively in the reaction of $Tm(NO_3)_3 \cdot 6H_2O$ and $K_2[Ni(CN)_4]$ (2:3 molar ratio). The structure is an extended array consisting of alternating Tm and Ni complexes where each Tm(III) cation is coordinated by five DMF molecules and a water molecule and Tm(III) ions are bridged by bidentate $Ni(CN)_4^{2-}$ anions. There is a $Ni(CN)_4^{2-}$ complex which serves as a link between two extended chains by hydrogen bond.^{8,9}

Experimental Section

General Procedures. All manipulations were carried out in a drybox under an atmosphere of dry, 99.99% pure nitrogen or on a high vacuum line. Dimethyl formamide (DMF; Aldrich) was stirred over pretreated 4 Å molecular sieves (Aldrich) for 4 days. The DMF was distilled into a 500 mL flask and then stored in the drybox for future use. $Tm(NO_3)_3 \cdot 6H_2O$ and $K_2[Ni(CN)_4]$ was purchased from Aldrich and used as received. Fourier transform infrared (FT-IR) spectra were recorded on a Mattson Polaris Fourier

transform spectrometer with 2 cm^{-1} resolution.

X-ray Structural Characterization. A single crystal of $\{(H_2O)_2(DMF)_{10}Tm_2[Ni(CN)_4]_2\}[Ni(CN)_4]$ was mounted on the tip of a glass fiber coated with Fomblin oil (Aldrich). Single crystal X-ray diffraction data were collected on an Enraf-Nonius Kappa-CCD diffraction system, which employs graphite monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å). Unit cell parameters were obtained by indexing the peaks in the first 10 frames and refined employing the whole data set. Data integration was done with Denzo, and scaling and merging of the data was done with Scalepack.¹⁰ The structure was solved by the Patterson method in SHELXS-97.¹¹ Full matrix least-squares refinements based on F^2 were performed in SHELXL-97,¹² as incorporated in the WinGX package.¹³ The hydrogen atoms of the water molecule in the complex were located on a difference electron density map and added to the molecule fixed at these positions. They are not refined during the least-squares procedure of fitting the model to the data and so the O-H bond lengths do not have any error values associated with them.

Preparation of $\{(H_2O)_2(DMF)_{10}Tm_2[Ni(CN)_4]_2\}[Ni(CN)_4]$. A 50 mL flask was charged with 275.3 mg (1.0 mmol) of $Tm(NO_3)_3 \cdot 6H_2O$ and a magnetic stirring bar in the drybox. Then 25 mL of DMF was pipetted into the flask. To this solution was added 361.4 mg (1.5 mmol) of $K_2[Ni(CN)_4]$ and the flask was sealed with a fine-fritted vacuum line extractor. After all reactants were dissolved in DMF, the mixture was stirred at room temperature for 2 days. The solution was degassed. The volume of the solution was reduced to about 3 mL and then crystalline KNO_3 was removed by filtration. The solution was reduced further to 1 mL for crystallization. X-ray quality single crystals formed in several weeks. Yield: nearly quantitative. IR (KBr, cm^{-1}) 3550-2950 (m, br, ν_{OH}), 2170 (s, ν_{CN}), 2156 (s, ν_{CN}), 2139 (s, ν_{CN}), 2128 (s, ν_{CN}).

Results and Discussion

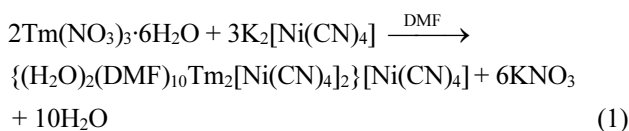
Cyanide-bridged Tm-Ni array with the general formula $\{(H_2O)_2(DMF)_{10}Tm_2[Ni(CN)_4]_2\}[Ni(CN)_4]$ was obtained quantitatively *via* metathesis reaction of 2 to 3 molar ratio of

Table 1. Crystallographic Data for $\{(H_2O)_2(DMF)_{10}Tm_2[Ni(CN)_4]_2\}[Ni(CN)_4]$

empirical formula	C ₄₂ H ₇₄ N ₂₂ Ni ₃ O ₁₂ Tm ₂
fw	1593.22
crystal system	triclinic
space group	Pi
a, Å	7.6095(1)
b, Å	9.7666(1)
c, Å	22.7764(2)
α, deg	86.423(1)
β, deg	81.935(1)
γ, deg	74.204(1)
V, Å ³	1612.17(5)
Z	1
Density ρ(calcd), mg/m ³	1.641
T, K	180(2)
λ, Å	Mo Kα(0.71073)
θ range (deg)	2.17-27.50
h k l ranges	-9 9, -12 12, -29 29
Reflections collected	41439
Independent reflections	7383
Absorption coefficient μ, mm ⁻¹	3.642
GOF	1.024
Final R indices [I > 2σ(I)] ^a	R ₁ = 0.0270, wR ₂ = 0.0586
R indices (all data) ^b	R ₁ = 0.0403, wR ₂ = 0.0624

^aR₁ = Σ||F_o - |F_c||/Σ|F_o|. ^bwR₂ = {Σw(F_o² - F_c²)²/Σw(F_o²)²}^{1/2}.

Tm(NO₃)₃·6H₂O with K₂Ni(CN)₄ in DMF at room temperature (Eq. 1). Single crystals formed in the reduced volume of the solution following crystalline KNO₃ removed.



Examination of the diffraction pattern showed a triclinic crystal system. Crystallographic data and selected bond distances and angles for $\{(H_2O)_2(DMF)_{10}Tm_2[Ni(CN)_4]_2\}[Ni(CN)_4]$ are listed in Tables 1 and 2, respectively. The molecular structure is an extended array of the cyanide-bridged lanthanide-transition metal hydrate complex consisting of alternative Tm and Ni atoms as shown in Figure 1. Within an array, each Tm atom is bonded to five O atoms (O1, O2, O3, O4, O5) of the DMF molecules, one O atom (O6) of water molecule, and two N atoms (N4, N6ⁱ) of the bridging cyanides of Ni(CN)₄ complexes. Two Tm atoms are bonded to a Ni(CN)₄ complex through cyanide bridges in a trans fashion. The coordination geometry around each of the thulium atoms can be described as a slightly distorted square antiprism. This is a common coordination geometry for eight-coordinated lanthanide complexes.¹⁴ One (N6ⁱ) of the two coordinated N atoms, two O atoms (O3, O5) and one O atom (O6) of water molecule occupy the corners of a base of the antiprism, while another coordinated N atom (N4) and three O atoms (O1, O2, O3) of DMF molecules occupy the

Table 2. Selected Bond Distances (Å) and Angles (deg)

Bond Distances			
Tm-O(1)	2.3408(19)	Tm-O(2)	2.281(2)
Tm-O(3)	2.3240(19)	Tm-O(4)	2.352(2)
Tm-O(5)	2.274(2)	Tm-O(6)	2.342(2)
Tm-N(4)	2.418(2)	Tm-N(6) ^{#1}	2.474(2)
Ni(1)-C(1)	1.867(3)	Ni(1)-C(2)	1.870(4)
Ni(2)-C(3)	1.875(3)	Ni(2)-C(4)	1.855(3)
Ni(2)-C(5)	1.876(3)	Ni(2)-C(6)	1.876(3)
N(1)-C(1)	1.149(4)	N(2)-C(2)	1.133(4)
N(3)-C(3)	1.146(4)	N(4)-C(4)	1.150(3)
N(5)-C(5)	1.140(4)	N(6)-C(6)	1.143(3)
O(6)-H(1O6)	0.842	O(6)-H(2O6)	0.808
Bond Angles			
O(1)-Tm-O(4)	125.41(8)	O(2)-Tm-N(4)	104.42(8)
O(3)-Tm-O(5)	110.88(9)	O(6)-Tm-N(6)	120.19(8)
O(1)-Tm-O(2)	73.58(7)	O(2)-Tm-O(4)	75.76(8)
O(1)-Tm-N(4)	75.13(8)	O(4)-Tm-N(4)	70.28(8)
O(1)-Tm-O(6)	73.91(7)	O(5)-Tm-O(6)	69.78(8)
O(3)-Tm-N(6)	71.43(7)	O(5)-Tm-N(6)	75.54(8)
Tm-N(4)-C(4)	175.9(2)	Tm ^{#3} -N(6)-C(6)	163.0(2)
C(3)-Ni(2)-C(4)	89.54(12)	C(4)-Ni(2)-C(5)	87.76(12)
C(3)-Ni(2)-C(5)	175.40(13)	C(4)-Ni(2)-C(6)	174.26(13)

Table 3. Hydrogen Bond Distances (Å) and D-A...H Bond Angles (deg, D = Donor, A = Acceptor) in $\{(H_2O)_2(DMF)_{10}Tm_2[Ni(CN)_4]_2\}[Ni(CN)_4]$

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(6)-H(1O6)N(5) ^{#4}	0.842	2.124	2.883(3)	149.8
O(6)-H(2O6)N(1) ^{#2}	0.808	1.967	2.762(4)	167.9

Symmetry transformations used to generate equivalent atoms: ^{#1}x+1, y-1, z ^{#2}-x+1, -y+2, -z+2 ^{#3}x-1, y+1, z ^{#4}x+1, y, z.

corners of another base of the antiprism. The average Tm-N, and Tm-O of DMF bond distances for the eight coordinate Tm(III) ion in the complex are 2.446, and 2.315 Å, respectively. The Tm-O of water bond distance is 2.342(2) Å. These distances are comparable to those observed in other Tm-M (M = transition metal) systems.⁷ Tm-N(4)-C(4) and Tm^{#3}-N(6)-C(6) angles are 175.9(2) and 163.0(2), respectively. The large deviation results from the steric crowding around N atoms. N(4) atom shares the edges of the square antiprism with one O atom of water molecule and three O atoms of DMF molecules, while N(6) atom shares the edges with four O atoms of DMF molecules.

The coordination geometry around the Ni atom is slightly distorted square planar.¹⁵ The Ni-C bond distance range 1.876(3) to 1.855(3) Å and the C-N bond distances range 1.150(3) to 1.140(4) Å. The *cis*-C-Ni(2)-C, and *trans*-C-Ni(2)-C bond angles range 93.22(12) to 87.76(12)°, and 175.40(13) to 174.26(13)°, respectively. The bond distances and angles are consistent with those of similar systems.¹⁶ There is a Ni(CN)₄ complex off by itself and this complex is involved in hydrogen bonding with the H₂O molecule bond-

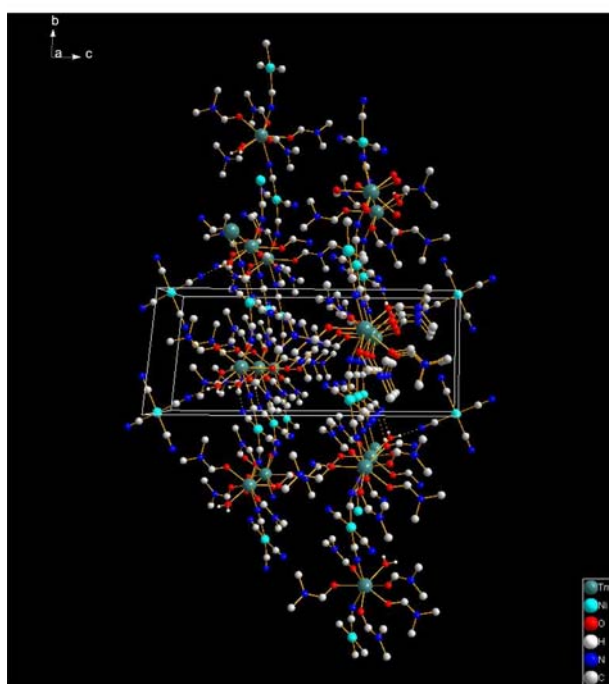
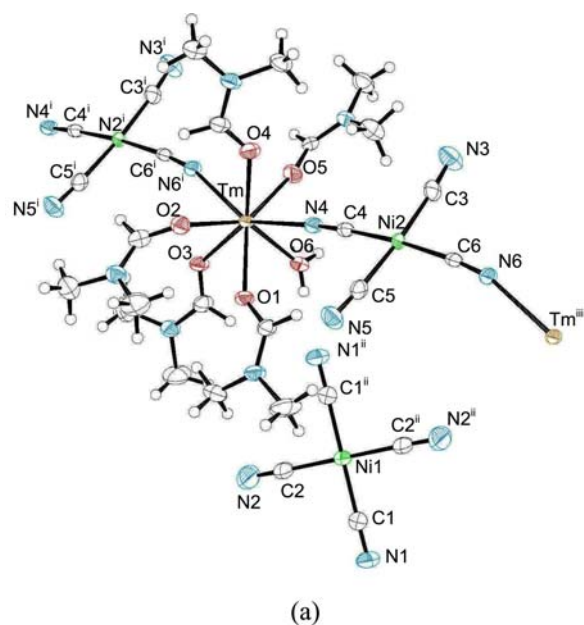


Figure 1. (a) ORTEP drawing (50% thermal ellipsoids) of $\{(H_2O)_2(DMF)_{10}Tm_2[Ni(CN)_4]_2\}[Ni(CN)_4]$ (b) An extended view of the stacking.

ed to Tm. Hence this $Ni(CN)_4$ complex, by virtue of its inversion center, serves as a link between two extended chains through this hydrogen bonding. The other hydrogen atom of this water molecule is involved in hydrogen bond with a CN group in a neighboring extended chain. Intermolecular hydrogen bond interactions between the polymers are shown in Figure 2. The distances of $H(106)N(5)^{\#4}$, and $H(206)N(1)^{\#2}$ are 2.124, and 1.967 Å, respectively. The angles of $O(6)-H(106)N(5)^{\#4}$, and $O(6)-H(206)N(1)^{\#2}$ are 149.8, and 167.9 Å, respectively. The HN distances are considerably shorter

than the van der Waals contact distance between H and N (2.55 Å), and $O-H \cdots N$ angles are considerably larger than 90° .¹⁷ Therefore, on the basis of these criteria, the close HN interactions in the complex should be accepted as hydrogen bonds.

The experimental section lists the observed infrared absorption frequencies for the complex. Typically bridging CN ligands have higher stretching frequencies than the terminal CN ligands.¹⁸ Accordingly, cyanide stretching bands (2170, 2156, 2139 cm^{-1}) at higher frequencies than the stretching band (2127 cm^{-1}) of $K_2[Ni(CN)_4]$ ¹⁹ are assigned to bridging cyanide ligands. The band at 2128 cm^{-1} is assigned to terminal cyanide ligands because their location in the cyanide stretching region compares with the absorption observed for the nonbridging cyanide ligands in $K_2[Ni(CN)_4]$. Array $\{(H_2O)_2(DMF)_{10}Tm_2[Ni(CN)_4]_2\}[Ni(CN)_4]$ and other lanthanide metal-Ni systems display similar CN stretching patterns in their spectra.⁶ A broad absorption band at 2950-3550 cm^{-1} was observed in the spectrum. This supports the presence of $O-H \cdots N$ intermolecular hydrogen bond interactions between the polymers.⁸

Supplementary Material. Crystallographic data for structural analysis have been deposited with the Cambridge Crystallographic Data Center (CCDC No. 873786). Copy of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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