

Synthesis and One Dimensional Structure of Novel Cyanide-Bridged Thulium-Palladium Heterobimetallic Complex $\{(\text{DMF})_{10}\text{Tm}_2[\text{Pd}(\text{CN})_4]_3\}_\infty$

Jang-Hoon Chung* and Sang Hern Kim†

Department of Chemistry, Myongji University, Yongin, Kyunggido 449-728, Korea. *E-mail: chungjh@mju.ac.kr

†Department of Applied Chemistry, Hanbat National University, Daejeon 305-719, Korea

Received September 7, 2005

Key Words : Lanthanide-transition heterobimetallic complex, One dimensional array

Heterometallic complexes containing both lanthanide and transition metals are of interest because they might serve as bimetallic catalysts or as precursors to bimetallic particles on oxide surfaces.¹ Direct lanthanide-transition metal bonds are ideal for such purposes. However, bonds between transition metals and electropositive elements such as lanthanides are relatively rare. Few such compounds have been structurally characterized.^{1b,2} Complexes with bridging ligands should be more accessible. Accordingly, investigations have mainly been limited to those containing the cyanide anion as a bridging ligand between lanthanide cations and the transition metals.^{3,4} The bidentate character of two of the four cyanides in $[\text{M}(\text{CN})_4]^{2-}$ has shown various types of structures in the solid state which are molecular,⁵ one-dimensional,^{4,6} or two-dimensional.⁷

In this study, we have investigated synthesizing ion-paired lanthanide-transition heterobimetallic complex using bridging cyanide ligand. Described here is recent work that led to the preparation and characterization of a novel one dimensional array a Tm(III) complex of the type $\{(\text{DMF})_{10}\text{Tm}_2[\text{Pd}(\text{CN})_4]_3\}_\infty$ prepared quantitatively from the reaction of TmCl_3 and $\text{K}_2\text{Pd}(\text{CN})_4$ (2 : 3 molar ratio). Here Tm(III) ions are bridged by the bidentate $\text{Pd}(\text{CN})_4^{2-}$ anions.

Experimental Section

General Procedures. All manipulations were carried out using a standard high vacuum line or in a drybox under an atmosphere of pure nitrogen. DMF (Baker) was stirred over pretreated 4 Å molecular sieves for 4-5 days. The DMF was distilled into a 1000 mL flask and then stored in the drybox. TmCl_3 was purchased from Strem and used as received. $\text{K}_2[\text{Pd}(\text{CN})_4] \cdot 3\text{H}_2\text{O}$ (Aldrich) was dried under vacuum at 200 °C for 1 h and stored in the drybox. ¹³C NMR spectra were recorded on a Bruker AM-250 NMR spectrometer operating at 62.90 MHz. Chemical shifts for ¹³C NMR spectra were internally referenced to carbon-13 peaks (δ (TMS) = 0.00). Fourier transform Infrared spectra were recorded on a Mattson Polaris Fourier Transform Spectrometer with 2 cm⁻¹ resolution. Samples were prepared in the drybox and analyzed as films placed between KBr plates in a airtight sample holder. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

X-ray Structural Characterization. Single crystal X-ray

diffraction data were collected on an Enraf-Nonius Kappa CCD diffraction system, which employs graphite monochromated Mo K α radiation ($\lambda = 0.71073$ Å). A single crystal of $\{(\text{DMF})_{10}\text{Tm}_2[\text{Pd}(\text{CN})_4]_3\}_\infty$ was mounted on the tip of a glass fiber coated with Fomblin oil (pentafluoropolyether), and crystallographic data were collected at -43 °C. Unit cell parameters were obtained by indexing the peaks in the first 10 frames and refined employing the whole data set. All frames were integrated and corrected for Lorentz and polarization effects using the Denzo-SMN package (Nonius BV, 1999).⁸ The empirical absorption correction was applied using the SORTAV program⁹ provided by MaXus software.¹⁰ The structure was solved by direct methods and refined using SHELXL-97 (difference electron density calculations and full matrix least-squares refinements) structure solution package.¹¹

Preparation of $\{(\text{DMF})_{10}\text{Tm}_2[\text{Pd}(\text{CN})_4]_3\}_\infty$. In the drybox, 275.3 mg (1.0 mmol) of TmCl_3 was dissolved in dry DMF. To this solution was added 577.5 mg (2.0 mmol) of $\text{K}_2\text{Pd}(\text{CN})_4$ and the mixture was stirred at room temperature for 5 days. During the process the solution turned cloudy due to the formation of KCl. The precipitate was removed by filtration, and the yellow filtrate was reduced in volume for crystallization. Crystals began to form during dynamic vacuum in a day. Yield: nearly quantitative. IR (KBr, ν_{CN} , cm⁻¹) 2181 (s), 2164 (s), 2138 (s), 2023 (w); ¹³C{¹H} NMR (DMF, 303 K) 170 ppm; Anal. Calcd for $\text{C}_{42}\text{H}_{70}\text{N}_{22}\text{O}_{10}\text{Pd}_3\text{Tm}_2$: C, 29.67; H, 4.15; N, 18.12. Found: C, 29.38; H, 3.93; N, 17.89.

Results and Discussion

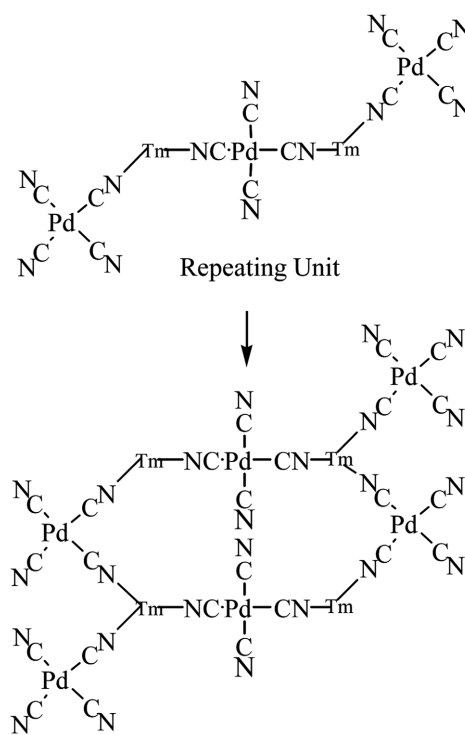
One dimensional array of heterobimetallic complex of the general formula $\{(\text{DMF})_{10}\text{Tm}_2[\text{Pd}(\text{CN})_4]_3\}_\infty$ was obtained via metathesis reaction of 2 : 3 molar ratio of TmCl_3 with $\text{K}_2\text{Pd}(\text{CN})_4$ in DMF at room temperature (eq. 1).



To ensure complete removal of chloride as KCl, long reaction time of 5 days was employed. The required long metathesis reaction time was in part due to the stability of the inner-sphere coordination complex.¹² The low solubility

of TmCl_3 in DMF also contributed to the long reaction time in the synthesis of the complex. A single crystal of the complex was obtained in 24 h after removal of DMF under high vacuum until a viscous solution resulted.

The crystal structure shows the general formula $\{(\text{DMF})_{10}\text{Tm}_2[\text{Pd}(\text{CN})_4]_3\}_8$ with one dimensional array. Crystallographic data and selected bond distances and angles are listed in Table 1 and 2, respectively. The repeating unit of the complex (Scheme 1) is translated only along the crystallographic a axis of the lattice. The structure consists of two parallel running zigzag chains that are inverted from each other. They are generated by two $\text{Pd}(\text{CN})_4^{2-}$ ions bridging Tm(III) ions in cis fashion. The chains are linked by a series of $\text{Pd}(\text{CN})_4^{2-}$ ions bridging the Tm atoms in a trans fashion. The Tm(III) ions are bound to three N and five O atoms of the bridging cyanide ions and DMF molecules, respectively, resulting in slightly distorted square antiprism. Two of the coordinated N atoms share an edge of one of the bases of the antiprism, while the third N atom occupies a corner of the other base opposite the shared edge. Average Tm-N bond distances are 2.450 while the average Tm-O bond distances are 2.320 Å. The average Tm-N and Tm-O bond distances are comparable to those observed in other lanthanide metal



Scheme 1

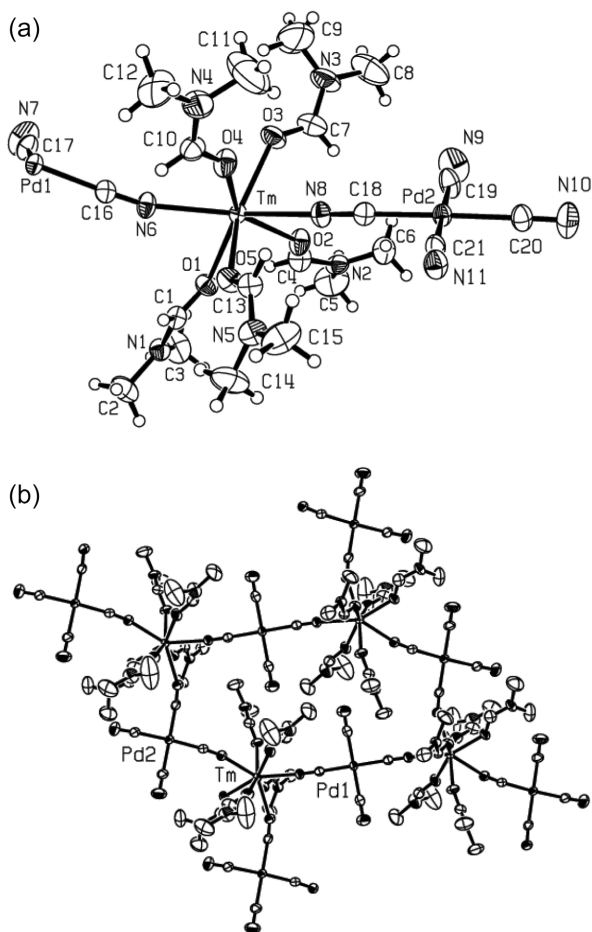


Figure 1. One dimensional structure (50% thermal ellipsoids) of $\{(\text{DMF})_{10}\text{Tm}_2[\text{Pd}(\text{CN})_4]_3\}_\infty$. (a) Coordination geometry around thulium atom. (b) A portion of one dimensional array.

system.¹³ The coordination geometry around the palladium atom is approximately square planar. The widest C-Pd-C bond angle is $92.35(14)$ (C18-Pd2-C21) that bridges in a cis fashion to two sterically crowded thulium atoms. To bridge these two thulium atoms, the C18-Pd2-C21 is opened, and thus this affects the linearity of the M-CN bond ranging from $156.8(3)$ to $169.4(3)^\circ$. This is most likely due to steric crowding around the Tm(III) cation.

The infrared spectrum (Figure 2) for the complex contains bands that are higher than the normal mode for the cyanide ligand in $\text{K}_2[\text{Pd}(\text{CN})_4]$ (2134 cm^{-1}).¹⁴ They are assigned to bridging cyanide stretching frequencies. Typically bridging CN ligands have higher stretching frequencies than the terminal CN ligands.¹⁵ The remaining CN stretching fre-

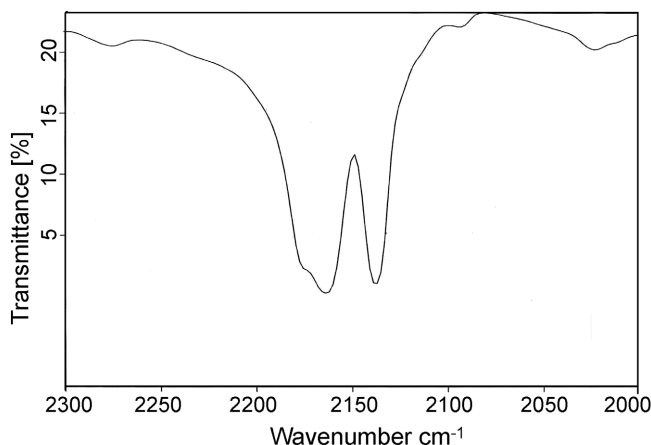


Figure 2. Infrared spectrum of $\{(\text{DMF})_{10}\text{Tm}_2[\text{Pd}(\text{CN})_4]_3\}_\infty$.

Table 1. Crystallographic Data for $\{(DMF)_{10}Tm_2[Pd(CN)_4]_3\}_\infty$

empirical formula	C ₄₂ H ₇₀ N ₂₂ O ₁₀ Pd ₃ Tm ₂
fw	1700.26
space group	P1
a, Å	9.205(1)
b, Å	11.744(1)
c, Å	16.157(2)
a, deg	80.009(4)
β , deg	74.480(4)
γ , deg	80.573(4)
V, Å ³	1644.7(3)
Z	1
ρ (calcd), g/cm ³	1.717
T, K	230(2)
λ , Å	Mo K α (0.71073)
θ range (deg)	2.06–27.46
<i>h k l</i> ranges	–11 11, –15 15, –20 20
Reflections collected	45023
Independent reflections	7490
μ , mm ^{–1}	3.536
GOF	1.101
R_1 [$I > 2\sigma(I)$] ^a	0.0300
wR_2 (all data) ^b	0.0663

$$^a R_1 = \sum \|F_o - |F_c|\| / \sum |F_o|, \quad ^b wR_2 = \{\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)\}^{1/2}.$$

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

Bond Distances			
Tm–O(1)	2.356(2)	Tm–O(2)	2.315(2)
Tm–O(3)	2.292(2)	Tm–O(4)	2.286(3)
Tm–O(5)	2.327(2)	Tm–N(6)	2.418(3)
Tm–N(8)	2.461(3)	Tm–N(11)#2	2.470(3)
Pd(1)–C(16)	1.995(4)	Pd(1)–C(17)	1.990(4)
Pd(2)–C(18)	1.995(4)	Pd(2)–C(19)	1.995(4)
Pd(2)–C(20)	1.996(4)	Pd(2)–C(21)	2.002(4)
N(6)–C(16)	1.140(4)	N(7)–C(17)	1.139(5)
N(8)–C(18)	1.148(5)	N(9)–C(19)	1.132(5)
N(10)–C(20)	1.135(5)	N(11)–C(21)	1.145(4)
Bond Angles			
C(17)–Pd(1)–C(17)#1	180.0(2)	C(19)–Pd(2)–C(20)	88.96(15)
C(17)–Pd(1)–C(16)#1	89.38(15)	C(18)–Pd(2)–C(21)	92.35(14)
C(17)#1–Pd(1)–C(16)#1	190.62(15)	C(19)–Pd(2)–C(21)	177.44(16)
C(17)–Pd(1)–C(16)	90.62(15)	C(20)–Pd(2)–C(21)	90.07(14)
C(17)#1–Pd(1)–C(16)	89.38(15)	C(16)–N(6)–Tm	164.9(3)
C(16)#1–Pd(1)–C(16)	180.0	C(18)–N(8)–Tm	169.4(3)
C(18)–Pd(2)–C(19)	88.70(15)	C(21)–N(11)–Tm#3	156.8(3)
C(18)–Pd(2)–C(20)	176.75(15)		

Symmetry transformations used to generate equivalent atoms: #1 $-x, -y, -z+1$ #2 $x-1, y, z$ #3 $x+1, y, z$

quencies are attributed to the nonbridging cyanide ligands because their location in the cyanide stretching region compares with the absorptions observed for the nonbridging

cyanide ligands in $K_2[Pd(CN)_4]$. The solid state structure of the complex differs from its solution structure. If nonfluctuational structure exists in solution, the $^{13}C\{^1H\}$ NMR spectrum of the complex should display multiple resonances due to both terminal and bridging cyanide ligands. However, the $^{13}C\{^1H\}$ NMR spectrum at room temperature shows only one resonance. The solution NMR data clearly indicates that ionization occurs and ion-paired species $Pd(CN)_4^{2-}$ including only terminal cyanide ligands exist. This is consistent with other system of Pd one dimensional array.¹³

Acknowledgement. This work was supported (in part) by the Korea Institute of Industrial Technology Evaluation & Planning (ITEP) through the Advanced Materials Research Center for Better Environment (AMAREN) at Hanbat National University.

Supplementary material. Crystallographic data for structural analysis have been deposited with the Cambridge Crystallographic Data Center (CCDC No. 281284). 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).

References

- (a) White, J. P., III; Deng, H. B.; Boyd, E. P.; Gallucci, J.; Shore, S. G. *Inorg. Chem.* **1994**, *33*, 1685. (b) Deng, H. B.; Shore, S. G. *J. Am. Chem. Soc.* **1991**, *113*, 8538.
- Beletskaya, I. P.; Voskoboynikov, A. Z.; Chuklanova, E. B.; Kirillova, N. I.; Shestakova, A. K.; Parshina, I. N.; Gusev, A. I.; Magomedov, G. K.-I. *J. Am. Chem. Soc.* **1993**, *115*, 3156.
- Deng, H.; Chun, S.; Florian, P.; Grandinetti, P. J.; Shore, S. G. *Inorg. Chem.* **1996**, *35*, 3891.
- (a) Knoepfel, D. W.; Shore, S. G. *Inorg. Chem.* **1996**, *35*, 1747. (b) Knoepfel, D. W.; Shore, S. G. *Inorg. Chem.* **1996**, *35*, 5328.
- Cernak, J.; Chomic, J.; Dunaj-Jurco, M. *Chem. Papers* **1990**, *44*, 13.
- Cernak, J.; Potocnak, I.; Chomic, J.; Dunaj-Jurco, M. *Acta Crystallogr.* **1990**, *C46*, 1098.
- Yuge, H.; Iwamoto, T. *Acta Crystallogr.* **1995**, *C51*, 374.
- Otwinowski, Z.; Minor, W. In *Methods in Enzymology*; Carter, C. W., Jr., Sweet, R. M., Eds.; Academic Press: New York, 1997; Vol. 276(A), p 307.
- (a) Blessing, R. H. *Acta Crystallogr., Sect. A* **1995**, *51*, 33. (b) Blessing, R. H. *J. Appl. Crystallogr.* **1997**, *30*, 421.
- Mackay, S.; Gilmore, C. J.; Edwards, C.; Tremayne, M.; Stuart, N.; Shankland, K. *MaXus: A Computer Program for the Solution and Refinement of Crystal Structures from Diffraction Data*; University of Glasgow: Scotland; Nonius BV: Delft, The Netherlands and Mac-Science Co. Ltd.: Yokohama, Japan, 1998.
- Sheldrick, G. M. *SHELXL-97: A Structure Solution and Refinement Program*; University of Göttingen: Germany, 1998.
- Ishiguro, S.; Takahashi, R. *Inorg. Chem.* **1991**, *30*, 1854.
- Knoepfel, D. W.; Liu, J.; Meyers, E. A.; Shore, S. G. *Inorg. Chem.* **1998**, *17*, 4828.
- Kubas, G. J.; Jones, L. H. *Inorg. Chem.* **1974**, *13*, 2186.
- Nakamodo, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds, Part B*, 5th ed; Wiley and Sons: New York, 1997; pp 105–113 and references therein.