

Synthesis and Structural Characterization of Novel Thulium-Platinum Heterobimetallic Complex $\{(\text{DMF})_{10}\text{Tm}_2[\text{Pt}(\text{CN})_4]_3\}_\infty$

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 Received November 15, 2006

Key Words : Thulium-platinum heterobimetallic complex, One dimensional array, Bridging cyanide

Lanthanide-transition heterobimetallic complexes have been intensively investigated because they can be employed as precursors in preparation of various materials such as oxide fuel cells,¹ electroceramic² and fluorescent materials,³ chemical sensor materials⁴ and catalysts.⁵ Incorporation of different metal atoms into the heterometallic complex may be accomplished through the formation of metal-metal bonds, or bridging ligands. Direct metal bonds between transition metals and electropositive lanthanide metals are relatively rare⁵ and the heterobimetallic complexes with bridging ligands should be more accessible. The cyano groups of $[\text{M}(\text{CN})_4]^{2-}$ can be used as bidentate ligands which bridge metal atoms.^{7,8} Therefore, the heterobimetallic complexes containing cyanide-bridged lanthanide-transition metal arrays have been of interest.

Recently, we reported the Tm-Pd heterobimetallic complex $\{(\text{DMF})_{10}\text{Tm}_2[\text{Pd}(\text{CN})_4]_3\}_\infty$ ⁹ and have focused on the syntheses of a series of thulium-group VIII transition metal complexes using bridging cyanide ligand. Here we describe the preparation and the structural characterization of a novel one dimensional array Tm(III)-Pt heterobimetallic complex of the type $\{(\text{DMF})_{10}\text{Tm}_2[\text{Pt}(\text{CN})_4]_3\}_\infty$ prepared quantitatively from the reaction of TmCl_3 and $\text{K}_2\text{Pt}(\text{CN})_4$ (2:3 molar ratio). In this complex, Tm(III) ions are bridged by the bidentate $\text{Pt}(\text{CN})_4^{2-}$ anions.

Experimental Section

General procedures. All manipulations were carried out using a standard high vacuum line or in a drybox under an atmosphere of nitrogen. Dimethyl formamide (DMF; Aldrich) 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 Aldrich and used as received. $\text{K}_2[\text{Pt}(\text{CN})_4] \cdot 3\text{H}_2\text{O}$ (Aldrich) was dried under vacuum at 200 °C for 1 h and stored in the drybox. 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 an airtight sample holder. Elemental analysis was performed by Galbraith

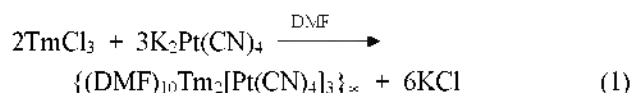
Laboratories, Inc., Knoxville, TN.

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 $\{(\text{DMF})_{10}\text{Tm}_2[\text{Pt}(\text{CN})_4]_3\}_\infty$ was mounted on the tip of a glass fiber coated with Fomblin oil (pentafluoropolyether). Unit cell parameters were obtained by indexing the peaks in the first 10 frames and refined employing the whole data set. Data integration was carried out for Lorentz and polarization effects using the Denzo-SMN package (Nonius BV, 1999).¹⁰ The absorption corrections were applied using the SORTAV program¹¹ provided by MaXus software.¹² 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.¹³

Preparation of $\{(\text{DMF})_{10}\text{Tm}_2[\text{Pt}(\text{CN})_4]_3\}_\infty$. In a drybox, 275.3 mg (1.0 mmol) of TmCl_3 was dissolved in dry DMF in a 50 mL flask equipped with a Kontes Teflon stopcock and a magnetic stirring bar. To this solution was added 577.5 mg (2.0 mmol) of $\text{K}_2\text{Pt}(\text{CN})_4$. After all reactants were dissolved in DMF, 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. X-ray quality single crystals formed during dynamic vacuum in a day. Yield: nearly quantitative. IR (KBr, ν_{CN} , cm^{-1}) 2184 (s), 2167 (s), 2139 (s), 2025 (w); Anal. Calcd for $\text{C}_{42}\text{H}_{70}\text{N}_{22}\text{O}_{10}\text{Pt}_3\text{Tm}_2$: C, 25.66; H, 3.59; N, 15.67. Found: C, 22.92; H, 3.10; N, 15.14.

Results and Discussion

The metathesis reaction of 2:3 molar ratio of TmCl_3 with $\text{K}_2\text{Pt}(\text{CN})_4$ in DMF produces one dimensional array of hetero-bimetallic complex of the general formula $\{(\text{DMF})_{10}\text{Tm}_2[\text{Pt}(\text{CN})_4]_3\}_\infty$ at room temperature (eq. 1).



Long reaction time of 5 days was employed to ensure complete removal of chloride as KCl. The low solubility of TmCl_3 in DMF also contributed to the long reaction time in the synthesis of the complex. The required long metathesis reaction time was in part due to the stability of the inner-sphere coordination complex.¹⁴

Crystallographic data and selected bond distances and angles are listed in Table 1 and 2, respectively. The crystal structure shows the general formula $\{(\text{DMF})_{10}\text{Tm}_2[\text{Pt}(\text{CN})_4]_3\}_\infty$ with one dimensional array. This structure is consistent with Tm-Pd system.⁹ The repeating unit of the complex in 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 $\text{Pt}(\text{CN})_4^{2-}$ ions bridging Tm(III) ions in cis fashion. The chains are linked by a series of $\text{Pt}(\text{CN})_4^{2-}$ ions bridging the Tm atoms in a trans fashion. The Tm(III) ions are bound to three N atoms of the bridging cyanides and five O atoms of 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 and Tm-O bond distances are 2.448 and 2.312 Å, respectively. These average distances are comparable to those observed in Tm-Pd and other lanthanide metal system.^{9,15} The coordination geometry around the platinum atom is approximately square planar. The widest C-Pt-C bond angle is 92.40(12) (C18-Pt2-C21) that bridges in a cis fashion to two sterically crowded thulium atoms. To bridge these two thulium atoms, the C18-Pt2-C21 is opened, and thus this affects the linearity of the M-CN bond ranging from 155.7(2) to 168.9(2)°. This is most likely due to steric crowding around the Tm(III)

Table 1. Crystallographic Data for $\{(\text{DMF})_{10}\text{Tm}_2[\text{Pt}(\text{CN})_4]_3\}_\infty$

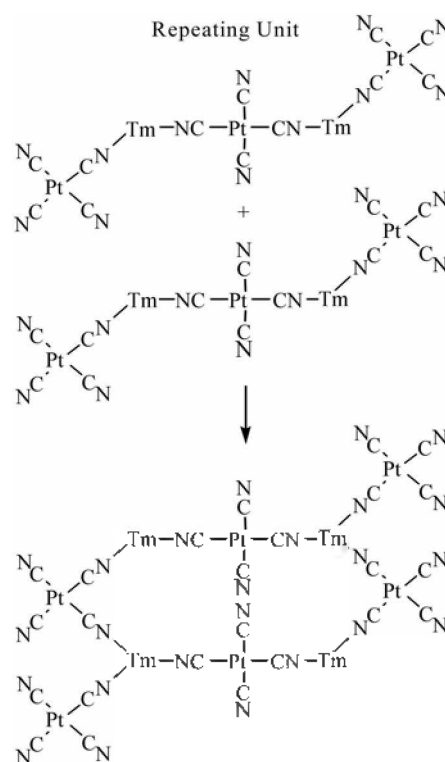
empirical formula	$\text{C}_{42}\text{H}_{70}\text{N}_{22}\text{O}_{10}\text{Pt}_3\text{Tm}_2$
fw	1966.33
space group	P1
a, Å	9.183(1)
b, Å	11.703(1)
c, Å	16.184(1)
α , deg	79.858(3)
β , deg	74.818(3)
γ , deg	80.877(5)
V, Å ³	1640.7(2)
Z	1
ρ (calcd), mg/m ³	1.990
T, K	230(2)
λ , Å	Mo K α (0.71073)
θ range (deg)	2.06-27.49
h k l ranges	-11 11, -15 15, -21 21
Reflections collected	41377
Independent reflections	7515
μ , mm ⁻¹	9.111
GOF	1.088
R_1 [$I > 2\sigma(I)$] ^a	0.0195
wR_2 (all data) ^b	0.0427

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

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

Bond Distances	
Tm-O(1) 2.352(2)	Tm-O(2) 2.311(2)
Tm-O(3) 2.288(2)	Tm-O(4) 2.283(3)
Tm-O(5) 2.324(2)	Tm-N(6) 2.413(3)
Tm-N(8) 2.465(3)	Tm-N(11)#2 2.465(3)
Pt(1)-C(16) 1.985(3)	Pt(1)-C(17) 1.991(4)
Pt(2)-C(18) 1.988(3)	Pt(2)-C(19) 1.990(3)
Pt(2)-C(20) 2.002(3)	Pt(2)-C(21) 1.996(3)
N(6)-C(16) 1.145(4)	N(7)-C(17) 1.138(4)
N(8)-C(18) 1.146(4)	N(9)-C(19) 1.141(4)
N(10)-C(20) 1.139(4)	N(11)-C(21) 1.148(4)
Bond Angles	
C(17)-Pt(1)-C(17)#1	180.0
C(17)-Pt(1)-C(16)#1	89.41(13)
C(17)#1-Pt(1)-C(16)#1	90.59(13)
C(17)-Pt(1)-C(16)	90.59(13)
C(17)#1-Pt(1)-C(16)	89.41(13)
C(16)#1-Pt(1)-C(16)	180.0(15)
C(18)-Pt(2)-C(19)	89.18(13)
C(18)-Pt(2)-C(20)	177.07(13)
C(19)-Pt(2)-C(20)	88.75(14)
C(18)-Pt(2)-C(21)	92.40(12)
C(19)-Pt(2)-C(21)	177.45(13)
C(20)-Pt(2)-C(21)	89.74(13)
C(16)-N(6)-Tm	165.1(3)
C(18)-N(8)-Tm	168.9(2)
C(21)-N(11)-Tm#3	155.7(2)

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



Scheme 1

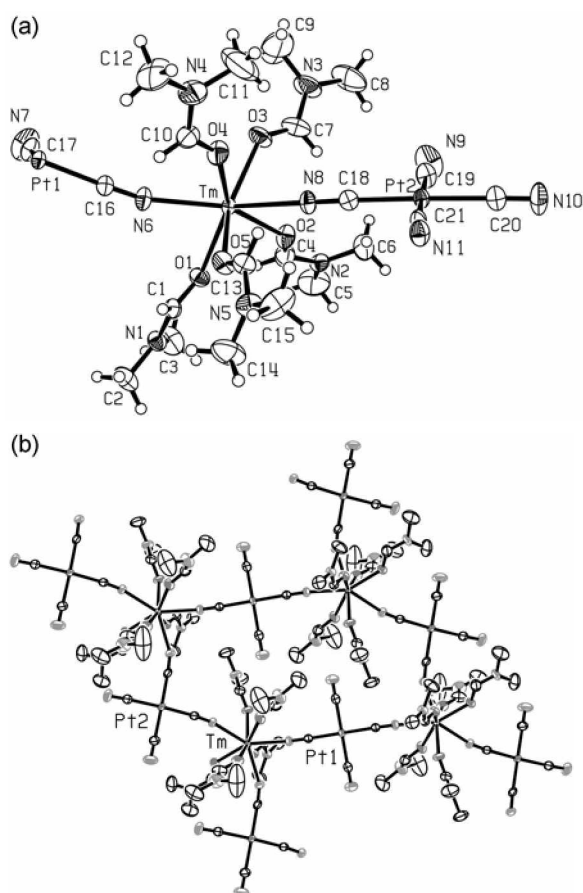


Figure 1. One dimensional structure (50% thermal ellipsoids) of $\{(\text{DMF})_{10}\text{Tm}_2[\text{Pt}(\text{CN})_4]_3\}_n$. (a) Coordination geometry around thulium atom. (b) A portion of one dimensional array.

cation.

The experimental section lists the observed infrared absorption frequencies for the complex. Arrays $\{(\text{DMF})_{10}\text{Tm}_2[\text{Pt}(\text{CN})_4]_3\}_n$ and Tm-Pd system complex $\{(\text{DMF})_{10}\text{Tm}_2[\text{Pd}(\text{CN})_4]_3\}_n$ display similar CN stretching patterns in their spectra of Figure 2. Cyanide stretching bands at higher

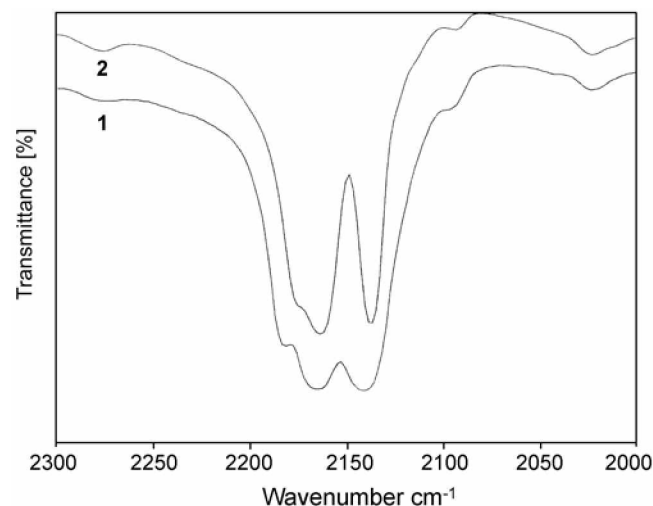


Figure 2. Infrared spectra of complex 1 $\{(\text{DMF})_{10}\text{Tm}_2[\text{Pt}(\text{CN})_4]_3\}_n$ and complex 2 $\{(\text{DMF})_{10}\text{Tm}_2[\text{Pd}(\text{CN})_4]_3\}_n$.

frequencies than the stretching modes of $\text{K}_2[\text{Pt}(\text{CN})_4] \cdot 3\text{H}_2\text{O}$ (2134 cm^{-1})¹⁶ are assigned to bridging cyanide ligands. Typically bridging CN ligands have higher stretching frequencies than the terminal CN ligands.¹⁷ The band occurs at around 2134 cm^{-1} is assigned to terminal cyanide ligands because their location in the cyanide stretching region compares with the absorptions observed for the nonbridging cyanide ligands in $\text{K}_2[\text{Pt}(\text{CN})_4] \cdot 3\text{H}_2\text{O}$.

Supplementary material. Crystallographic data for structural analysis have been deposited with the Cambridge Crystallographic Data Center (CCDC No. 283317). 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](http://www.ccdc.cam.ac.uk)).

Acknowledgement. We thank Dr. Judith Gallucci in the Department of Chemistry of The Ohio State University for providing the crystal structure results.

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