An Unusual Cyanide Bridging Lanthanide−Transition Metal Complex that Contains the One-Dimensional Cationic Array $\{[(DMF)_{16}Yb_6(\mu_6\text{-}O)(\mu_3\text{-}OH)_8(\mu\text{-}NC)Pd(\mu\text{-}CN)(CN)_2]^{6+}\}_\infty$

Jianping Liu, Edward A. Meyers, and Sheldon G. Shore*

Department of Chemistry, The Ohio State University, Columbus, Ohio 43210

Received May 11, 1998

A new type of lanthanide−group 10 transition metal mixed ligand complex, $\{[(DMF)_{16}Yb_6(\mu_6\text{-}O)(\mu_3\text{-}OH)_8(\mu\text{-}NC)Pd(\mu\text{-}CN)(CN)_2][Pd(CN)_4]_3\cdot 4DMF\}_\infty$, has been produced through the redox reaction of $YbCl_2$ with $K_2[Pd(CN)_4]\cdot H_2O$ in DMF.[1] It is the first example, to our knowledge, of a cationic chain array in which hydroxo-lanthanide clusters are linked through bridging transition metal anion complexes. In this reaction Yb^{2+} was oxidized to Yb^{3+} and the protons in water were reduced to H_2. The resulting ionic species in the presence of $[Pd(CN)_4]^{2-}$ in DMF solution yielded colorless crystals and also light yellow crystals. The colorless crystals are $\{[(DMF)_8(H_2O)_2Yb_2[Pd(CN)_4]_3\cdot 0.26H_2O\}_\infty$, whose structure is similar to a type we designated as type **A** and reported earlier[2c] except that two DMF molecules are replaced by two H_2O molecules. It is not discussed here. But its structural information is included in the Supporting Information. The light yellow crystals are the title complex which is discussed below.

Figure 1[3] depicts the packing in the unit cell of the title complex. It contains a portion of the cationic, chainlike array $\{[(DMF)_{16}Yb_6(\mu_6\text{-}O)(\mu_3\text{-}OH)_8(\mu\text{-}NC)Pd(\mu\text{-}CN)(CN)_2]^{6+}\}_\infty$ with three $[Pd(CN)_4]^{2-}$ counterions. The chain consists of clusters of

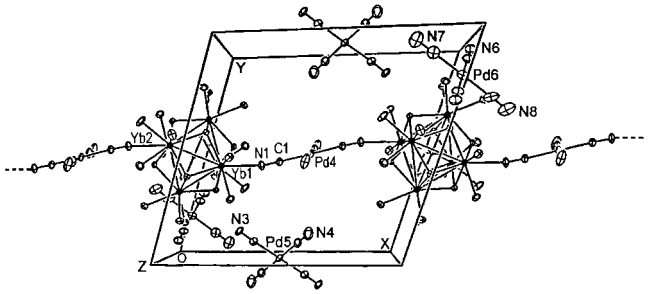

Figure 1. Unit cell packing diagram showing extend infinite chain in the complex $\{[(DMF)_{16}Yb_6(\mu_6\text{-}O)(\mu_3\text{-}OH)_8(\mu\text{-}NC)Pd(\mu\text{-}CN)(CN)_2][Pd(CN)_4]_3\cdot 4DMF\}_\infty$ with 25% thermal ellipsoids. The center of the unit is chosen at (1, 1, 0), only oxygen atoms in DMF are displayed, and cocrystallized DMF solvent molecules are omitted for clarity. Selected bond lengths (Å): Yb1−N1, 2.424(7); Yb−O (OH^- groups), 2.270(5)−2.343(5); Yb−O(interstitial oxygen atom), 2.413(1)−2.450(1); Yb−O(DMF molecules), 2.270(7)−2.405(7); Pd−C, 1.97(2)−2.02(2); C−N(cyanide groups), 1.11(2)−1.16(2). Selected bond angles (deg): O(OH^- groups)−Yb−O(OH^- groups), 73.4(2)−89.7(2) and 129.4(2)−131.6(2); Yb−O(interstitial oxygen atom)−Yb, 88.84(3)-91.16(3); Yb−O(OH^- groups)−Yb, 94.4(2)−98.5(2); C−Pd−C, 89.2(5)−90.8(5); Pd−C−N, 177(1)−179(1); Yb−N−C, 166.4(9).

$[(DMF)_{16}Yb_6(\mu_6\text{-}O)(\mu_3\text{-}OH)_8]^{8+}$ that are linked through the trans cyanide ligands of $[Pd(CN)_4]^{2-}$ in which nitrogen atoms in cyanide ligands form dative bonds with ytterbium centers. Each repeating unit $[(DMF)_{16}Yb_6(\mu_6\text{-}O)(\mu_3\text{-}OH)_8(\mu\text{-}NC)Pd(\mu\text{-}CN)(CN)_2]^{6+}$ carries a +6 charge that is offset by three square planar $[Pd(CN)_4]^{2-}$ anions. Four DMF solvent molecules per unit cell are also cocrystallized in the unit cell. The core of the cluster (Figure 2) contains an interstitial O^{2-} ion that is octahedrally coordinated to six Yb^{3+} cations. This $Yb_6(\mu_6\text{-}O)$ unit is located within a cubic arrangement of eight OH^- anions, each of which caps a triangular face of the octahedron and is coordinated to each of the three Yb^{3+} cations that define the face. Although the hydrogen atoms were not located by X-ray analysis, the solid-state IR spectrum of the crystals reveals the O−H stretching vibration at 3656 cm^{-1}.[4] External to the cube-octahedral core, there are ligands of DMF and cyano groups bound to the Yb^{3+} cations. Each Yb^{3+} has distorted dodecahedral coordination geometry. Four of these cations are each coordinated to three terminal DMF ligands, four OH^- units, and the central O^{2-} anion. The remaining two Yb^{3+} cations are also coordinated to the central O^{2-}, but one of the DMF ligands on each cation is replaced by a cyano group.

The infrared spectrum of $\{[(DMF)_{16}Yb_6(\mu_6\text{-}O)(\mu_3\text{-}OH)_8(\mu\text{-}NC)Pd(\mu\text{-}CN)(CN)_2][Pd(CN)_4]_3\cdot 4DMF\}_\infty$ (KBr pellet) in the CN stretching region consists of two bands. The band at 2139 cm^{-1}

(1) In the drybox, 48.8 mg (0.20 mmol) of $YbCl_2$ and 57.5 mg (0.19 mmol) of $K_2[Pd(CN)_4]\cdot H_2O$ were added to a 15 mL of dry[2] DMF. An orange solution was formed. The mixture was stirred 15 days at ambient temperature under an N_2 atmosphere, and then the mixture was filtered, leaving a white precipitate (KCl) on the frit and an orange filtrate. The color of the solution changed gradually from orange to light yellow upon the removal of the DMF from the filtrate, and a yellowish viscous oil was formed. After 24 h, light yellow and colorless crystals formed that were manually separated. The light yellow crystals were $\{[(DMF)_{16}Yb_6(\mu_6\text{-}O)(\mu_3\text{-}OH)_8(\mu\text{-}NC)Pd(\mu\text{-}CN)(CN)_2][Pd(CN)_4]_3\cdot 4DMF\}_\infty$ (10 mg, 8.5% yield based on $YbCl_2$). IR (KBr pellet, cm^{-1}): ν_{OH} 3656 (m), ν_{CN} 2161 (s), 2139 (s), $\nu_{O(DMF)-Yb}$ 684 (s), the rest of absorption bands belong to DMF molecules: 2993 (m), 2818 (w), 1666 (vs), 1496 (m), 1437 (s), 1420 (sh, m), 1385 (s), 1252 (m), 1116 (s), 1061 (w), 1019 (w), 866 (w). IR (DMF, cm^{-1}): 2167 (m), 2142 (m), 2135 (s), 2126 (vs). The colorless crystals were $\{[(DMF)_8(H_2O)_2Yb_2[Pd(CN)_4]_3\cdot 0.26H_2O\}_\infty$ (50 mg, 31% yield based on $YbCl_2$). IR (KBr pellet, cm^{-1}): ν_{water} 3400 (br, m), ρ_r 801 (m), ν_{CN} 2179 (sh, s), 2170 (vs), 2147(sh, s), 2141 (vs), $\nu_{O(DMF)-Yb}$ 682 (s), the rest of absorption bands belong to DMF molecules: 2961 (w), 2933 (m), 1662 (vs), 1506 (m), 1437 (s), 1420 (sh, m), 1379 (s), 1252 (m), 1109 (s), 1060 (m), 1016 (w), IR(DMF, cm^{-1}): 2167 (m), 2142 (m), 2135 (s), 2126 (vs).

(2) (a) Knoeppel, D. W.; Shore. S. G. *Inorg. Chem.* **1996**, *35*, 1747. (b) Knoeppel, D. W.; Shore. S. G. *Inorg. Chem.* **1996**, *35*, 5328. (c). Knoeppel, D. W.; Liu, J.; Meyers, E. A.; Shore. S. G. *Inorg. Chem.* **1998**, *37*, 4828.

(3) Diffraction data were collected with an Enraf-Nonius CAD4 diffractometer using Mo Kα radiation. All data were corrected for Lorentz and polarization and empirical absorption effects. Crystallographic computations were carried out using the SHELXTL software package. Structure solutions involved a DIRECT method. Crystal data for $\{[(DMF)_{16}Yb_6(\mu_6\text{-}O)(\mu_3\text{-}OH)_8(\mu\text{-}NC)Pd(\mu\text{-}CN)(CN)_2][Pd(CN)_4]_3\cdot 4DMF\}_\infty$ (−60 °C): space group *P*1, $a = 14.871(5)$ Å, $b = 14.931(5)$ Å, $c = 17.289(4)$ Å, $\alpha = 65.23(1)°$, $\beta = 76.85(2)°$, $\gamma = 68.95(3)°$, $V = 3240(2)$ Å^3, fw = 3494.14, $Z = 2$, ρ(calcd) = 1.791 g/cm^3, $\mu = 4.897$ mm^{-1}, R_1 [$I > 2\sigma(I)$] = 0.0346 ($R_1 = \sum||F_o| - |F_c||/\sum|F_o|$), wR_2 (all data) = 0.144 39 ($wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$), and GooF = 1.188 (685 variable parameters refined) for 9609 reflections [$I > 2\sigma(I)$] of 11363 independent reflections ($4 \le 2\theta \le 50°$).

(4) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th ed.; John Wiley & Sons: New York, 1986; p 230.

10.1021/ic9805271 CCC: $15.00
Published on Web 09/30/1998

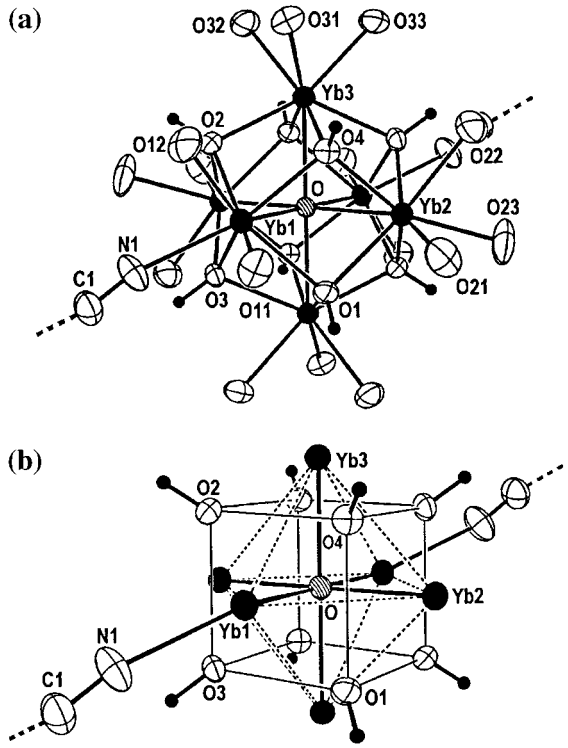

Figure 2. (a) Molecular structure of $[(DMF)_{16}Yb_6(\mu_6\text{-}O)(\mu_3\text{-}OH)_8]^{8+}$ cluster with 50% thermal ellipsoids. Only oxygen atoms of DMF molecules coordinated to ytterbium ions were shown for clarity. (b) Octahedral arrangement of Yb^{3+} ions and the cubic arrangement of OH^- groups.

is assigned to unbridged cyano groups in $[Pd(CN)_4]^{2-}$.[5] The band at 2161 cm^{-1} is assigned to the bridging CN^- groups.[4] The sharp band at 3656 cm^{-1} is in the range observed for the O−H stretching vibration.[4] The solution IR of this complex is different from its solid-state IR, indicating that the solid-state structure does not exist in solution.

The core of the $[Yb_6(\mu_6\text{-}O)(\mu_3\text{-}OH)_8)]$ in $\{[(DMF)_{16}Yb_6(\mu_6\text{-}O)(\mu_3\text{-}OH)_8(\mu\text{-}NC)Pd(\mu\text{-}CN)(CN)_2]^{6+}\}_\infty$ is similar to that of $[Yb_6(\mu_6\text{-}O)(\mu_3\text{-}OH)_8(H_2O)_{12}(NO_3)_6]^{2+}$ which is reported as the nitrate salt.[6] Structural parameters of the two clusters are in excellent agreement. In the present case $\{[(DMF)_{16}Yb_6(\mu_6\text{-}O)(\mu_3\text{-}OH)_8(\mu\text{-}NC)Pd(\mu\text{-}CN)(CN)_2][Pd(CN)_4]_3\cdot 4DMF\}_\infty$ is effectively a one-dimensional infinite array while the cation of the nitrate salt, $[Yb_6(\mu_6\text{-}O)(\mu_3\text{-}OH)_8(H_2O)_{12}(NO_3)_6]^{2+}$, exists in a hydrogen-bonded aggregate with a different type of coordination geometry around Yb^{3+}: a distorted tricapped trigonal prism consisting of four OH^- ligands, the interstitial O^{2-}, two H_2O molecules, and one bidentate NO_3^- anion.[6]

This cationic chainlike array described here raises the possibility of synthesizing similar arrays comprised of lanthanide-hydroxo clusters linked by bis-monodentate complex anions.

Acknowledgment. This work was supported by the National Science Foundation through Grant CHE97-00394.

Supporting Information Available: Listings of crystallographic data, atomic coordinates, and anisotropic thermal parameters for both $\{[(DMF)_{16}Yb_6(\mu_6\text{-}O)(\mu_3\text{-}OH)_8(\mu\text{-}NC)Pd(\mu\text{-}CN)(CN)_2][Pd(CN)_4]_3\cdot 4DMF\}_\infty$ and $\{[(DMF)_8(H_2O)_2Yb_2[Pd(CN)_4]_3\cdot 0.26H_2O\}_\infty$ and molecular structure of $\{[(DMF)_8(H_2O)_2Yb_2[Pd(CN)_4]_3\cdot 0.26H_2O\}_\infty$ (23 pages). Ordering information is given on any current masthead page.

IC9805271

(5) Kubas, G. J.; Jones, L. H. *Inorg. Chem.* **1974**, *13*, 2816.
(6) Žák, Z.; Unfried, P.; Giester, G. *J. Alloys Compounds* **1994**, *205*, 235.