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Crystallographic report

(η^5-Fluorenyl)-tris-pyridine-di-iodo-lanthanum(III) and -neodymium(III)

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The structures of the title compounds are mononuclear with each lanthanide bound by a single η^5-fluorenyl ligand, two trans-disposed iodides and three meridionally oriented pyridine molecules.

KEYWORDS: crystal structure; fluorenyl; lanthanum; neodymium

COMMENT

In contrast to the pentamethylcyclopentadienyl ligand, fluorenyl complexes of the lanthanides remain scarce.[1–7] Even more rare are mono-fluorenyl lanthanide species, the sole example being the cationic ytterbium(II) derivative, [(fluorenyl)Yb(THF)$_4$][AlMe$_4$].[6] Previous attempts to prepare mono-fluorenyl lanthanide complexes by the 1 : 1 reaction of (fluorenyl)Li and $LnCl_3$ have been unsuccessful.[2,3] Here, we report the X-ray crystal structures of (η^5-fluorenyl)$LnI_2(py)_3$ (Ln = La (**1**), Nd (**2**)), which are the first examples of neutral, mono-fluorenyl complexes of the lanthanides. The geometry about the lanthanide center is pseudo-octahedral, with the iodides trans to each other and a meridional arrangement of pyridine molecules. The Ln–centroid and Ln–I distances are normal for compounds of this type (see Fig. 1 caption). The structures of **1** and **2** are similar to those reported for (η^5-C_5Me_5)$NdI_2(py)_3$[8] and (η^5-$C_5H_2(SiMe_3)_3$-1, 2, 4)$LaI_2(py)_3$.[9]

EXPERIMENTAL

A tetrahydrofuran (THF) solution of (fluorenyl)K (1.00 g, 4.89 mmol) was added to a solution of LaI_3THF_4 (3.95 g, 4.89 mmol) in THF, forming a yellow–orange slurry. After stirring for 1 h, the slurry was filtered through Celite to remove KI, and the solvent was removed under vacuum. The yellow solid was dissolved in toluene and approx 1 ml of pyridine added. The solution was stirred for 30 min, forming

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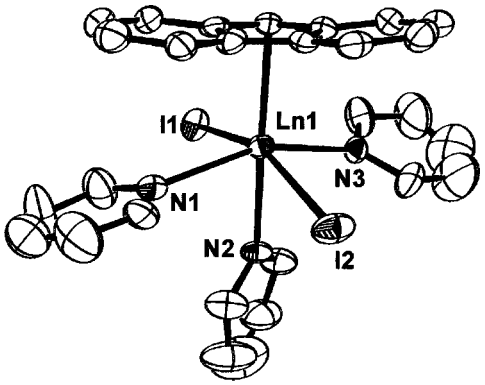

Figure 1. Molecular structure of (η^5-fluorenyl)$LnI_2(py)_3$ (Ln = La (**1**), Nd (**2**)). Key geometric parameters for **1**: La1–N1 2.655(4), La1–N2 2.755(5), La1–N3 2.684(4), La1–I1 3.2403(8), La1–I2 3.1738(9), La1–centroid 2.593 Å; I1–La1–I2 153.00(2), I1–La1–N1 87.87(9), I1–La1–N2 77.58(10), I1–La1–N3 85.44(9), I1–La1–centroid 100.64, I2–La1–N1 88.83(9), I2–La1–N2 78.64(10), I2–La1–N3 87.34(9), I2–La1–centroid 103.20, N1–La1–N2 74.47(14), N1–La1–N3 154.36(13), N1–La1–centroid 104.58, N2–La1–N3 79.92(13), N2–La1–centroid 177.93, N3–La1–centroid 100.98°. For **2**: Nd1–N1 2.518(6), Nd1–N2 2.592(6), Nd1–N3 2.563(5), Nd1–I1 3.1758(8), Nd1–I2 3.1334(8), Nd1–centroid 2.542 Å; I1–Nd1–I2 157.81(2), I1–Nd1–N1 87.5(1), I1–Nd1–N2 77.5(2), I1–Nd1–N3 87.5(1), I1–Nd1–centroid 100.16, I2–Nd1–N1 87.3(1), I2–Nd1–N2 86.5(1), I2–Nd1–N3 90.0(1), I2–Nd1–centroid 102.03, N1–Nd1–N2 77.3(2), N1–Nd1–N3 157.1(2), N1–Nd1–centroid 99.25, N2–Nd1–N3 79.9(2), N2–Nd1–centroid 175.68, N3–Nd1–centroid 103.58°.

a yellow slurry. The solvent was removed under vacuum, the solid washed with hexanes and dried under vacuum to yield **1** as a bright yellow solid (3.80 g, 98% yield). X-ray quality crystals were grown by slow evaporation of a saturated toluene solution. The neodymium derivative was prepared similarly, yielding green crystals of **2**.

Crystal data for **1**(toluene)$_{0.5}$ ($C_{31.5}H_{28}I_2LaN_3$): $M = 841.28$, $0.32 \times 0.20 \times 0.20$ mm^3, monoclinic, space group $P2_1/c$, $a = 10.210(4)$ Å, $b = 31.655(11)$ Å, $c = 19.183(7)$ Å, $\beta = 99.931(7)°$, $V = 6107(4)$ Å^3, $Z = 8$, $D_{calc} = 1.830$ g cm^{-3}. Bruker P4/CCD diffractometer, $T = 203(2)$ K, θ range = 1.26–25.43°, μ(Mo Kα) = 3.445 mm^{-1}, 38 517 reflections collected, 11 162 reflections with $I > 2\sigma(I)$. $R = 0.0582$ (obs. data), $wR_2 = 0.0953$ (all data). Programs used: SMART, SAINT, SADABS, SHELXTL NT, ORTEP3. CCDC deposition number: 238 126.

Crystal data for **2**(THF) ($C_{32}H_{32}I_2N_3NdO$): $M = 872.65$, $0.24 \times 0.20 \times 0.10$ mm^3, orthorhombic, space group *Pbcn*, $a = 18.765(6)$ Å, $b = 16.833(5)$ Å, $c = 19.955(6)$ Å, $V = 6303(3)$ Å^3, $Z = 8$, $D_{calc} = 1.839$ g cm^{-3}. Bruker P4/CCD diffractometer, $T = 203(2)$ K, θ range = 1.63–25.40°, μ(Mo Kα) = 3.635 mm^{-1}, 38 573 reflections collected, 5799 reflections with $I > 2\sigma(I)$. $R = 0.0600$ (obs. data), $wR_2 = 0.1157$ (all data). Programs used: SMART, SAINT, SADABS, SHELXTL NT, ORTEP3. CCDC deposition number: 238 127.

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