

## Supporting Information

### Oxidation and Coupling of $\beta$ -Diketiminato Ligand in Lanthanide Complexes: Novel Eight-Nuclear Lanthanide Cluster with $\mu$ -, $\mu_3$ -Cl, and $\mu_4$ -O Bridges

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## Experimental Section

**General Procedures.** All operations were performed under an inert atmosphere of nitrogen using standard Schlenk-line or glove-box techniques. The solvents of THF, toluene, *n*-hexane were refluxed and distilled over sodium benzophenone ketyl under nitrogen immediately prior to use.  $[\text{CH}\{(\text{Me})\text{C}=\text{NC}_6\text{H}_3\text{-}2,6\text{-}^i\text{Pr}\}_2]\text{LnCl}_2(\text{THF})_2$  (Ln = Er(**1**), Dy(**2**)) were prepared by slightly modified literature methods.<sup>1</sup> All other chemicals were commercially available and used after appropriate purification. Elemental analyses for C, H and N were carried out on a Rapid CHN-O analyzer. Infrared spectra were obtained on a NICOLET FT-IR 360 spectrometer with samples prepared as Nujol mulls. <sup>1</sup>H NMR data were obtained on a Brüker DMX-400 NMR spectrometer.

**Preparation of  $\text{Er}_8(\mu\text{-}\eta^2\text{-L}^4)_2(\mu_3\text{-Cl})_4(\mu\text{-Cl})_{10}(\mu_4\text{-O})_3(\text{THF})_8$  (**3**)** ( $\text{L}^4 = [\text{OC}\{(\text{Me})\text{CN-}2,6\text{-}^i\text{PrC}_6\text{H}_3\}_2]^{2-}$ ) and  $[\text{CH}\{(\text{Me})\text{C}=\text{N-}2,6\text{-}^i\text{PrC}_6\text{H}_3\}_2]_2$  (**5**). **1**  $\{[\text{CH}\{(\text{Me})\text{C}=\text{NC}_6\text{H}_3\text{-}2,6\text{-}^i\text{Pr}\}_2]\text{ErCl}_2(\text{THF})_2\}$  (1.05 g, 1.31 mmol) was dissolved in a 15 mL THF solution in a 80-mL Schlenk flask under nitrogen. Then the system was periodically filled with trace dried oxygen at room temperature during one week. (*Note: A 40mL O<sub>2</sub>, desiccated by calcium oxide, was injected into a 200-mL Schlenk flask under nitrogen. Then the two flasks (the 80-mL Schlenk flask and the 200-mL*

Schlenk flask) were connected by a latex line. The stopcocks of the two flasks were opened periodically for the diffusion of O<sub>2</sub>. This operation should be done for 5-6 times in a workday, and each time is about 30 minutes. The most difficult in these experiments is the perfect controlling of the concentration of O<sub>2</sub> in the 80-mL Schlenk flask.) The solution color changed slowly from pink to orange. The resulting solution was concentrated by reduced pressure to about 5 mL. Crystallization by vapor diffusion of *n*-hexane into the THF solution affords pink crystals **3**. Yield: 0.234 g (43 % based on Er). Anal. Calcd for C<sub>90</sub>H<sub>144</sub>N<sub>4</sub>O<sub>13</sub>Cl<sub>14</sub>Er<sub>8</sub>: C, 32.52; H, 4.37; N, 1.69. Found: C, 32.69; H, 4.53; N, 1.77. IR (Nujol, cm<sup>-1</sup>): 1624 m, 1591 w, 1553 m, 1508 s, 1310 s, 1257 m, 1172 m, 1040 s, 955 s, 872 m, 77 m, 693 w. The solvents of the above mother liquor were removed under vacuum, and the solid residue was extracted by *n*-hexane. The extract *n*-hexane solution was concentrated and cooled at -35 °C to give colorless crystals of **5**·0.5hexane. Yield: 0.212 g (37 %). C, H, N analysis (%): calcd for C<sub>61</sub>H<sub>89</sub>N<sub>4</sub>: C 83.41, H 10.21, N 6.38; found: C 83.34, H 10.16, N 6.47. <sup>1</sup>H NMR (DCCl<sub>3</sub> 7.25): δ 13.38 (s, 2H, NH) 7.12–7.10 (m, 12H, aromatic protons), δ 3.16 (m, 8H CH(CH<sub>3</sub>)<sub>2</sub>), δ 1.76 (s, 12H CH<sub>3</sub>), δ 1.14 (m, 48H CH(CH<sub>3</sub>)<sub>2</sub>).

**Synthesis of Dy<sub>8</sub>(μ-η<sup>2</sup>-L<sup>4</sup>)<sub>2</sub>(μ<sub>3</sub>-Cl)<sub>4</sub>(μ-Cl)<sub>10</sub>(μ<sub>4</sub>-O)<sub>3</sub>(THF)<sub>8</sub> (**4**) and **5**.** Using the same procedure described for **3**, Treatment of [CH{(Me)C=NC<sub>6</sub>H<sub>3</sub>-2,6-<sup>*i*</sup>Pr }<sub>2</sub>]DyCl<sub>2</sub>(THF)<sub>2</sub> (**2**) (0.779 g, 0.98 mmol) in THF at room temperature under an atmosphere of nitrogen with trace O<sub>2</sub> filled periodically over several days to gave **4** as pale yellow crystals and **5** as colorless crystals, respectively. Yield: **4**, 0.165 g (41%); **5**, 0.146 g (34%). Anal. Calcd for C<sub>90</sub>H<sub>144</sub>N<sub>4</sub>O<sub>13</sub>Cl<sub>14</sub>Dy<sub>8</sub> (**4**): C, 45.61; H, 5.85; N, 9.39. Found: C, 45.39; H, 5.71; N, 9.47. IR (Nujol, cm<sup>-1</sup>): 1622 m, 1592 w, 1552 m, 1507 s, 1308 s, 1254 m, 1174 m, 1037 s, 952 s, 869 m, 793 m, 690 w.

**Synthesis of O=C{(Me)CN-2,6-<sup>*i*</sup>PrC<sub>6</sub>H<sub>3</sub>}<sub>2</sub> (**6**).** To a solution of Cu<sup>II</sup>(CH<sub>3</sub>COO)<sub>2</sub>·H<sub>2</sub>O (300 mg, 1.50 mmol) in CH<sub>3</sub>OH-CH<sub>2</sub>Cl<sub>2</sub> (v/v = 4 : 1, 30 mL) was added dropwise a solution of **HL** (CH<sub>2</sub>{(Me)C=N-2,6-<sup>*i*</sup>PrC<sub>6</sub>H<sub>3</sub>}<sub>2</sub>) (0.628 g, 1.50 mmol) in CH<sub>3</sub>OH-CH<sub>2</sub>Cl<sub>2</sub> (v/v = 4 : 1, 30 mL) with stirring at room temperature. After stirring the mixture for 30 min, removal of the solvents gave a brown material, which was washed with water and collected by filtration. Then the brown powder was treated in

methanol (50 mL) at 50 °C for 12 h under O<sub>2</sub>. Reduction of the volume of solution to ca. 10 mL by evaporation, and standing the resulting solution for several hours gave a pale brown material (0.360 g, 64 %), from which single crystals of complex **6** was obtained by recrystallization from methanol. C, H, N analysis (%): calcd for C<sub>29</sub>H<sub>40</sub>ON<sub>2</sub>: C 80.51, H 9.32, N 6.48; found: C 80.43, H 9.26, N 6.62. <sup>1</sup>H NMR (DCCl<sub>3</sub> 7.25): δ 7.18–7.10 (m, 6H, aromatic protons), δ 2.81 (m, 4H CH(CH<sub>3</sub>)<sub>2</sub>), δ 1.98 (s, 6H CH<sub>3</sub>), δ 1.13 (m, 24H CH(CH<sub>3</sub>)<sub>2</sub>).

**X-ray Data Collection, Structure Determination and Refinement.** Suitable single crystals of complexes **3-6** were sealed under argon in Lindemann glass capillaries for X-ray structural analysis. Diffraction data were collected on a Bruker SMART Apex CCD diffractometer using graphite-monochromated MoK $\alpha$  ( $\lambda = 0.71073$  Å) radiation. During the intensity data collection, no significant decay was observed. The intensities were corrected for Lorentz-polarization effects and empirical absorption with SADABS program.<sup>2</sup> The structures were solved by the direct method using the SHELXL-97 program.<sup>3</sup> All non-hydrogen atoms were found from the difference Fourier syntheses. The H atoms were included in calculated positions with isotropic thermal parameters related to those of the supporting carbon atoms, but were not included in the refinement. All calculations were performed using the SHELXL program.

Crystallographic data for **3**: C<sub>90</sub>H<sub>144</sub>C<sub>114</sub>Er<sub>8</sub>N<sub>4</sub>O<sub>13</sub>, T = 293(2) K, M<sub>w</sub> = 3324.47, orthorhombic, space group Aba2, a = 28.632(4), b = 31.254(5), c = 16.142(2) Å, V = 14444(4) Å<sup>3</sup>, Z = 4, D<sub>c</sub> = 1.529 g cm<sup>-3</sup>,  $\mu(\text{Mo-K}\alpha) = 4.894$  mm<sup>-1</sup>, F(000) = 6392, 12510 reflections measured, 6617 unique (R<sub>int</sub> = 0.0405) which was used in all calculations. Final R1 = 0.0325 and wR2 = 0.0717 (I > 2  $\sigma$ ). CCDC 819597.

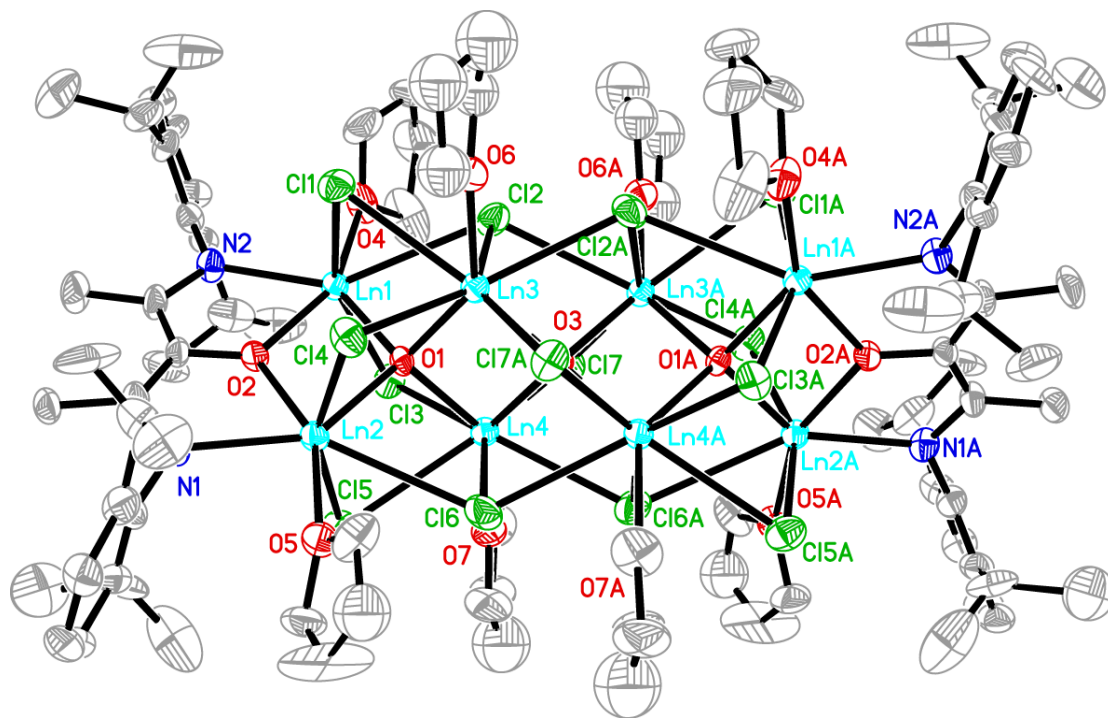
Crystallographic data for **4**: C<sub>90</sub>H<sub>144</sub>C<sub>114</sub>Dy<sub>8</sub>N<sub>4</sub>O<sub>13</sub>, T = 293(2) K, M<sub>w</sub> = 3286.39, orthorhombic, space group Aba2, a = 28.668(6), b = 31.282(6), c = 16.199(3) Å, V = 14527(5) Å<sup>3</sup>, Z = 4, D<sub>c</sub> = 1.503 g cm<sup>-3</sup>,  $\mu(\text{Mo-K}\alpha) = 4.359$  mm<sup>-1</sup>, F(000) = 6328, 12652 reflections measured, 6650 unique (R<sub>int</sub> = 0.0819) which was used in all calculations. Final R1 = 0.0490 and wR2 = 0.1078 (I > 2  $\sigma$ ). CCDC 819598.

Crystallographic data for **5**:  $C_{61}H_{89}N_4$ ,  $T = 293(2)$  K,  $M_w = 878.36$ , triclinic, space group  $P-1$ ,  $a = 12.937(4)$ ,  $b = 13.424(4)$ ,  $c = 17.464(6)$  Å,  $\alpha = 86.122(5)$ ,  $\beta = 75.906(5)$ ,  $\gamma = 71.960(5)^\circ$ ,  $V = 2796.9(16)$  Å<sup>3</sup>,  $Z = 2$ ,  $D_c = 1.043$  g cm<sup>-3</sup>,  $\mu(\text{Mo-K}\alpha) = 0.060$  mm<sup>-1</sup>,  $F(000) = 966$ , 11658 reflections measured, 9683 unique ( $R_{\text{int}} = 0.0346$ ) which was used in all calculations. Final  $R1 = 0.0555$  and  $wR2 = 0.1372$  ( $I > 2 \sigma$ ). CCDC 819599.

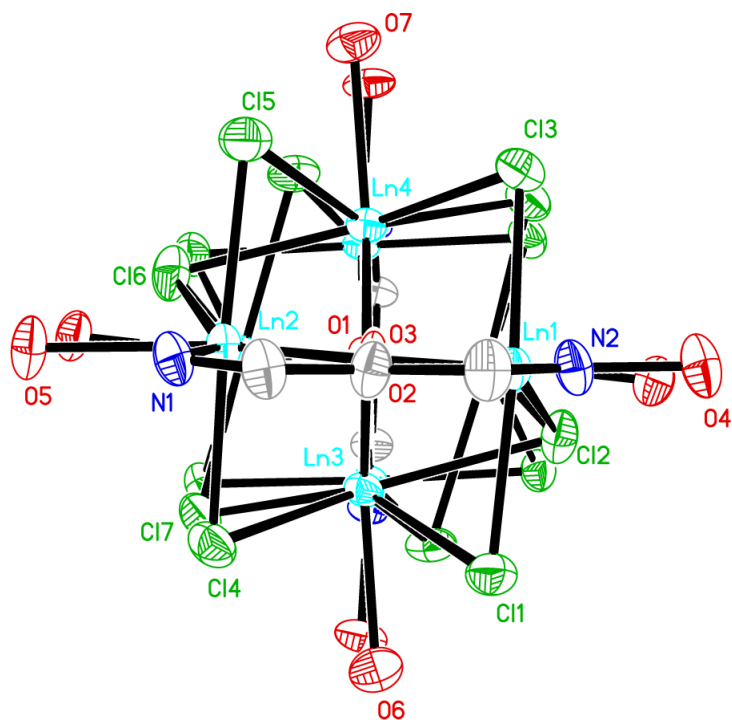
Crystallographic data or **6**:  $C_{29}H_{40}N_2O$ ,  $T = 293(2)$  K,  $M_w = 432.63$ , triclinic, space group  $P-1$ ,  $a = 9.177(5)$ ,  $b = 10.603(5)$ ,  $c = 15.394(8)$  Å,  $\alpha = 85.265(7)^\circ$ ,  $\beta = 73.552(7)^\circ$ ,  $\gamma = 66.988(6)^\circ$ ,  $V = 1321.5(11)$  Å<sup>3</sup>,  $Z = 2$ ,  $D_c = 1.087$  g cm<sup>-3</sup>,  $\mu(\text{Mo-K}\alpha) = 0.065$  mm<sup>-1</sup>,  $F(000) = 472$ , 5497 reflections measured, 4578 unique ( $R_{\text{int}} = 0.0651$ ) which was used in all calculations. Final  $R1 = 0.0932$  and  $wR2 = 0.2381$  ( $I > 2 \sigma$ ). CCDC 819590.

## References

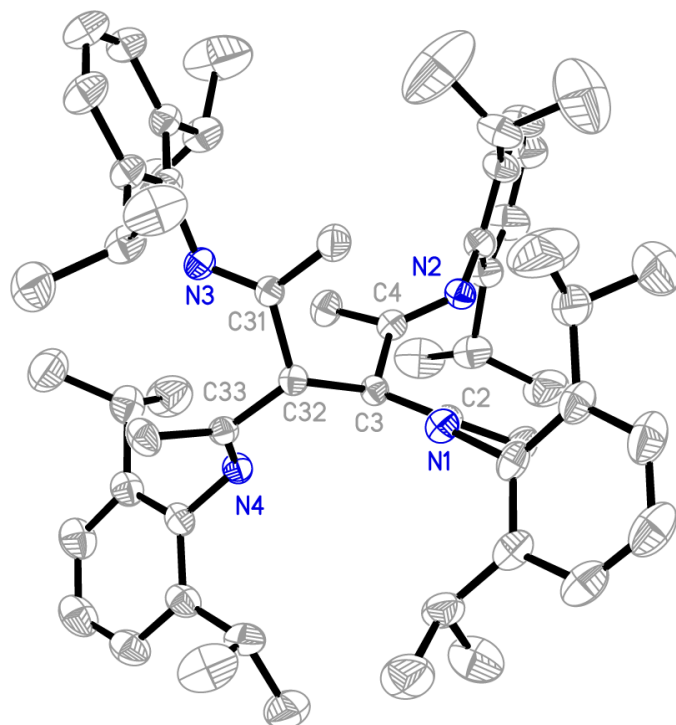
1. Cui, C.; Shafir, A.; Schmidt, J. A. R.; Oliver, A. G.; Arnold, J. *Dalton* **2005**, 1387.
2. Sheldrick, G. M. *SADABS, A Program for Empirical Absorption Correction*; Göttingen, Germany, 1998.
3. Sheldrick G. M., *SHELXL-97, Program for the refinement of the crystal structure*; University of Göttingen: Germany, 1997.



**Figure 1.** Molecular structure of **3** (Ln = Er) and **4** (Ln = Dy) with the probability ellipsoids drawn at the 30% level. Hydrogen atoms are omitted for clarity.

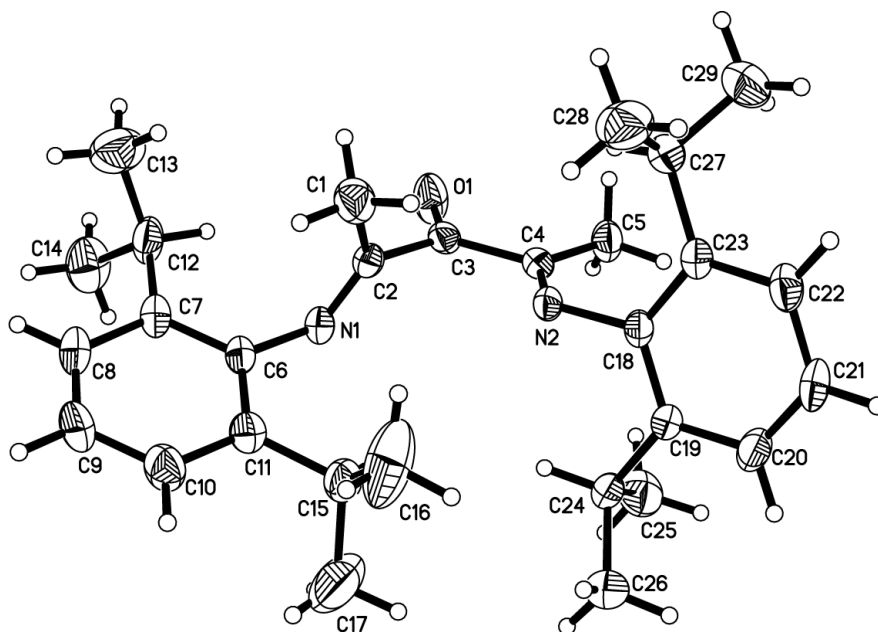


**Figure 2.** View of the core of **3** and **4** from the orientation of the oxygen axis.



**Figure 3.** Molecular structure of **5** with the probability ellipsoids drawn at the 30% level.

Hydrogen atoms are omitted for clarity.



**Figure 4.** Molecular structure of **6** with the probability ellipsoids drawn at the 30% level.  
Hydrogen atoms are omitted for clarity.