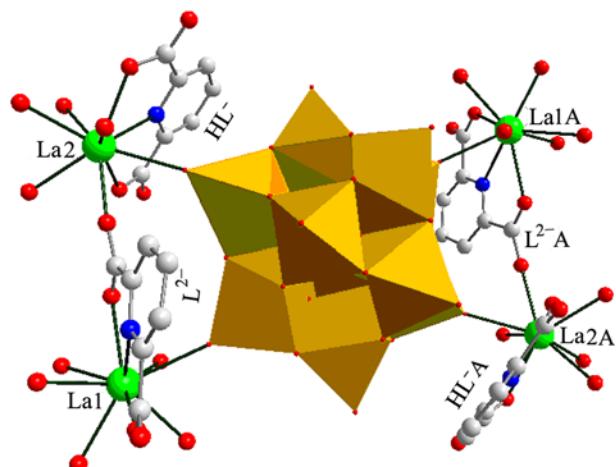


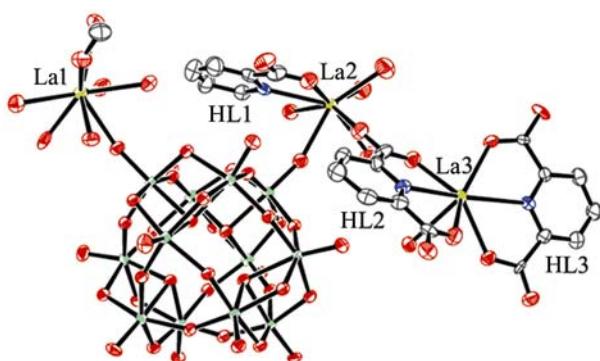
## Supporting information for <<2D and 3D Polyoxometalate-Based Rare Earth-Organic Frameworks: Toward the Design and Synthesis of High-Dimensional Framework>>

Mi-Xia Hu, Ya-Guang Chen,\* Chun-Jing Zhang, Hai-Jun Pang, and Qing-Jiao Kong

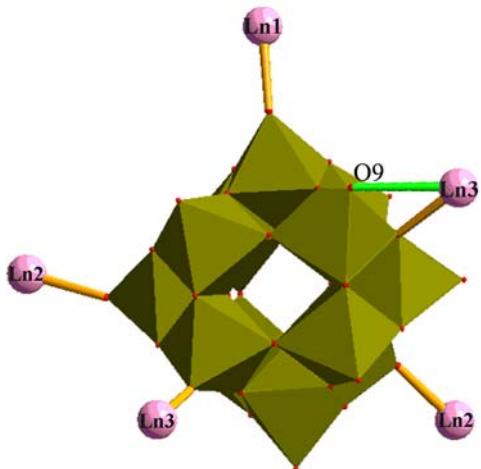
*Key Lab of Polyoxometalate Science, Department of Chemistry, Northeast Normal University, Changchun 130024, People's Republic of China*  
*E-mail:chengy146@nenu.edu.cn*



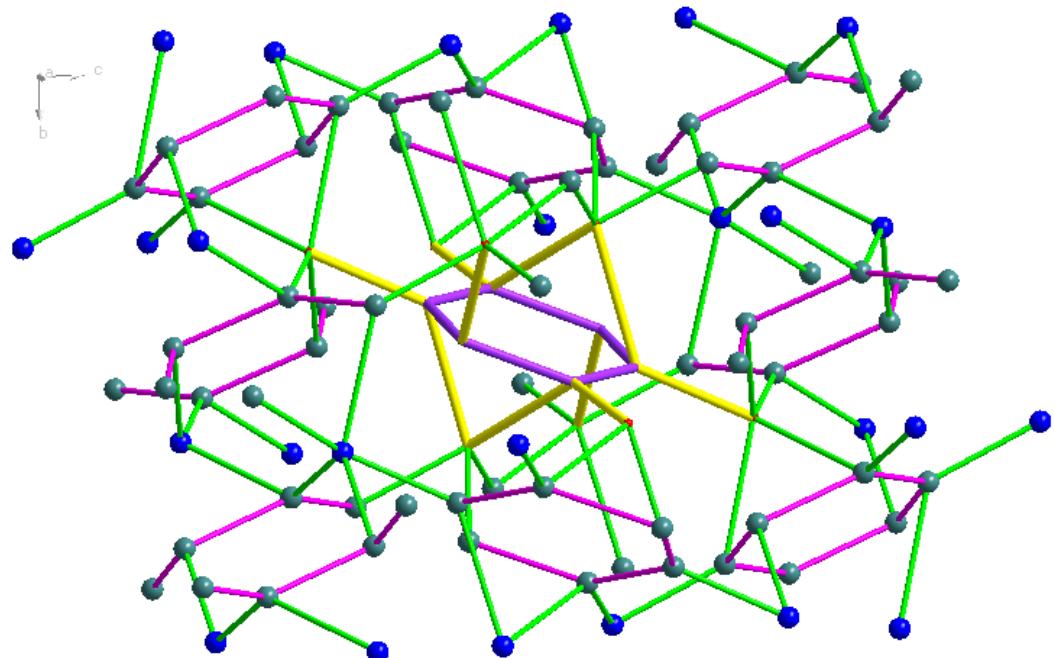
**Figure S1.** Polyhedral and ball-and-stick representation of the basic unit of **1**. The hydrogen atoms and crystal water molecules are omitted for clarity.



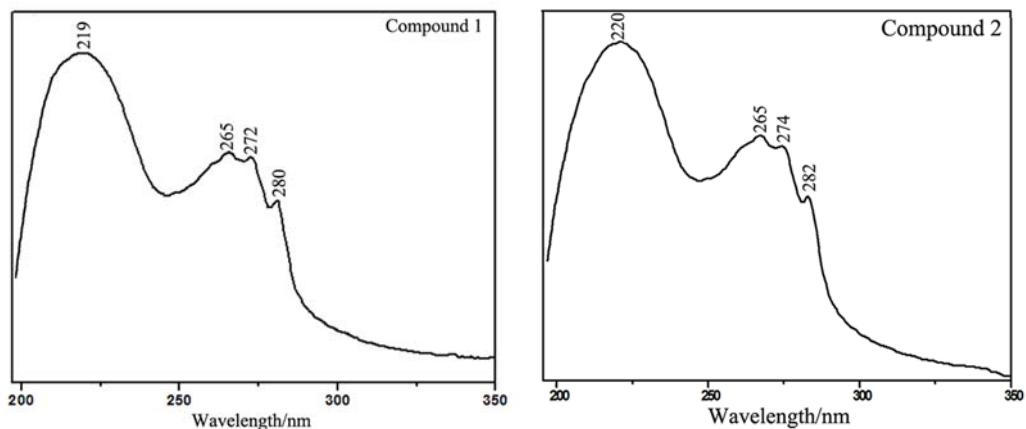
**Figure S2.** ORTEP drawing of **5**. The hydrogen atoms and crystal water molecules are omitted for clarity.



**Figure S3.** The coordination sites of  $\text{W}_{12}$  cluster in **5–8** (the green link is only for **5** and **6**).

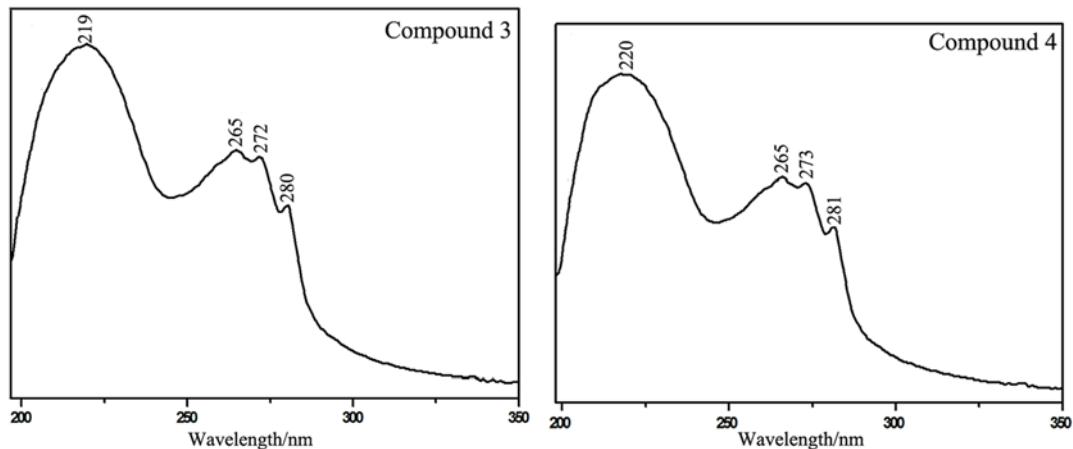


**Figure S4.** The detailed connection of 2D layer. .



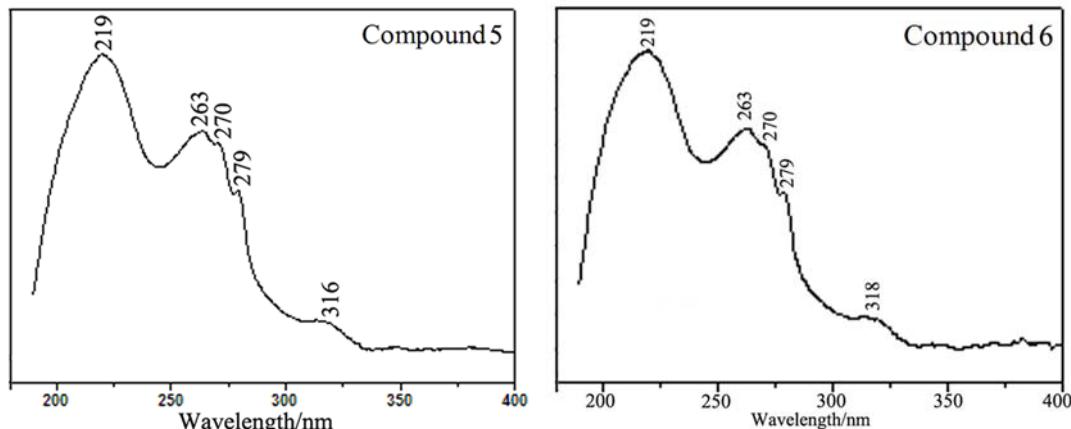
**Figure S5.** The UV spectrum for 1.

**Figure S6.** The UV spectrum for 2.



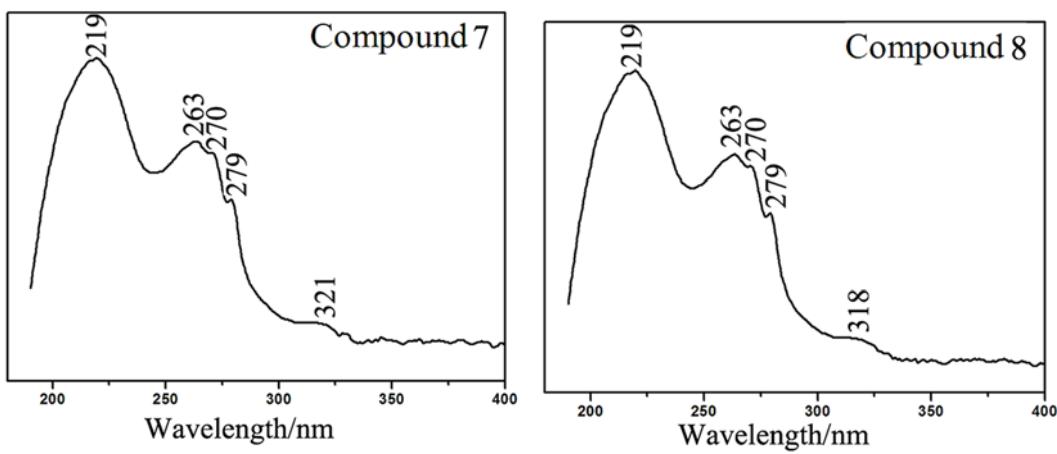
**Figure S7.** The UV spectrum for 3.

**Figure S8.** The UV spectrum for 4.



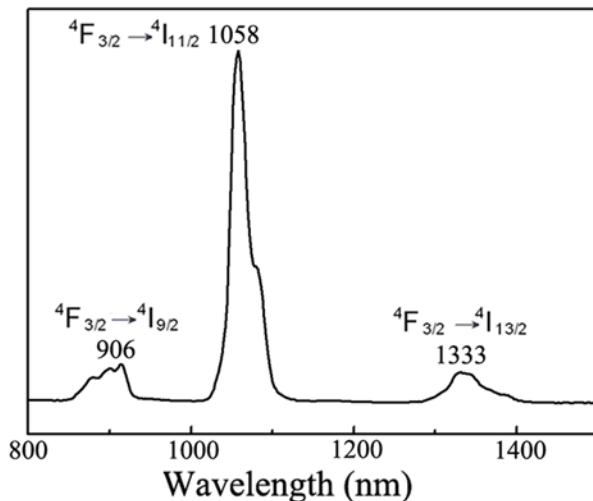
**Figure S9.** The UV spectrum for 5.

**Figure S10.** The UV spectrum for 6.

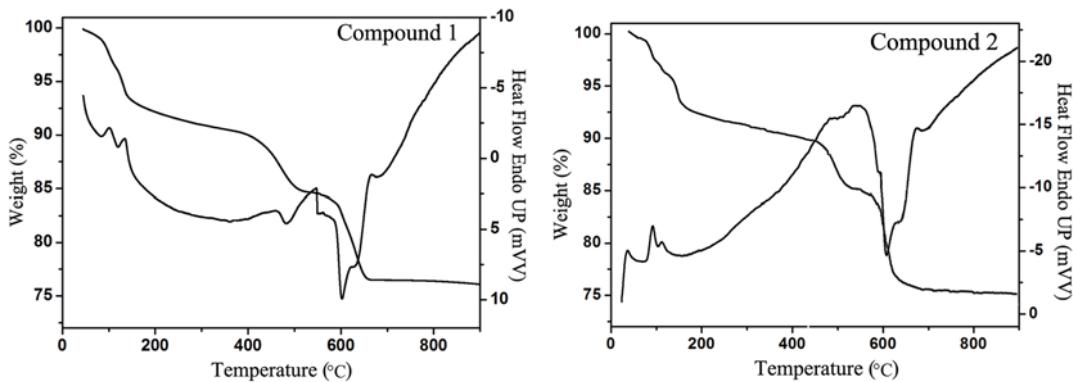


**Figure S11.** The UV spectrum for **7**.

**Figure S12.** The UV spectrum for **8**.

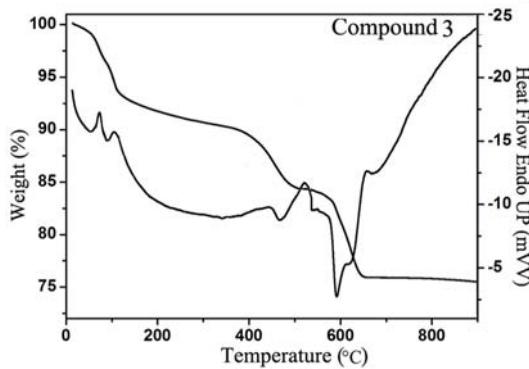


**Figure S13.** Solid-state emission spectrum of **8** excited at 517 nm.

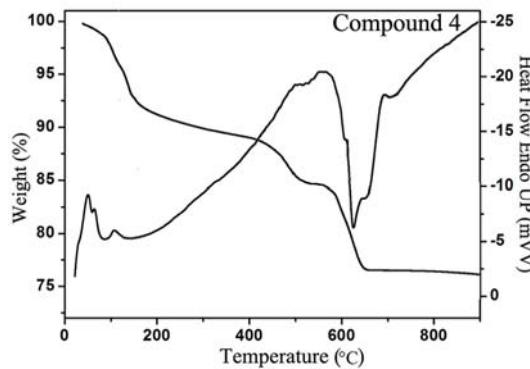


**Figure S14.** The TG curve for **1**.

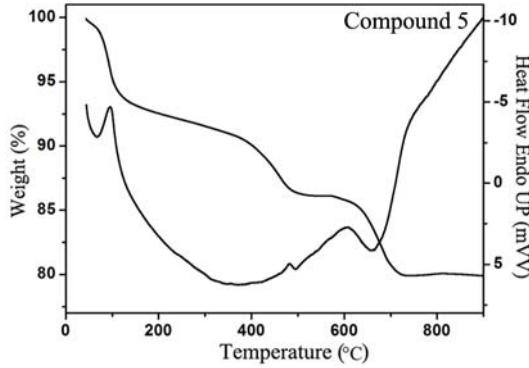
**Figure S15.** The TG curve for **2**.



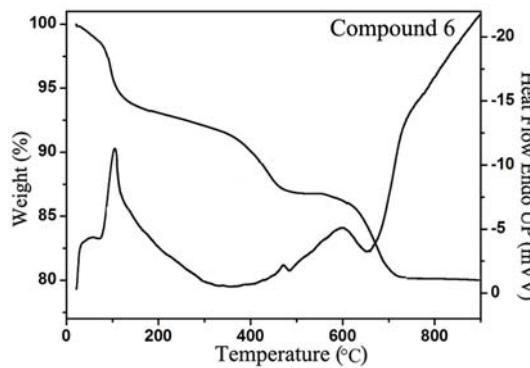
**Figure S16.** The TG curve for 3.



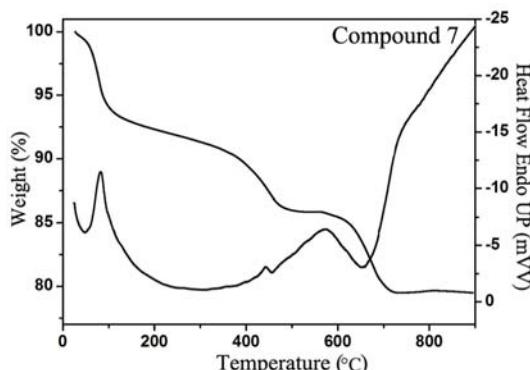
**Figure S17.** The TG curve for 4.



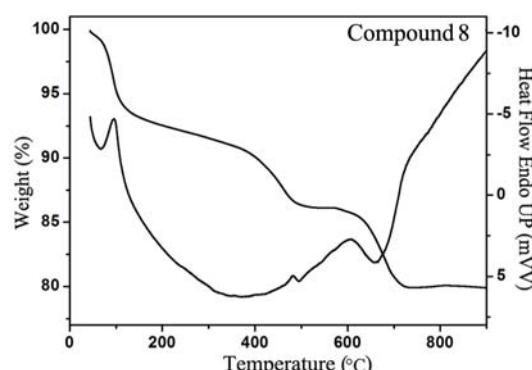
**Figure S18.** The TG curve for 5.



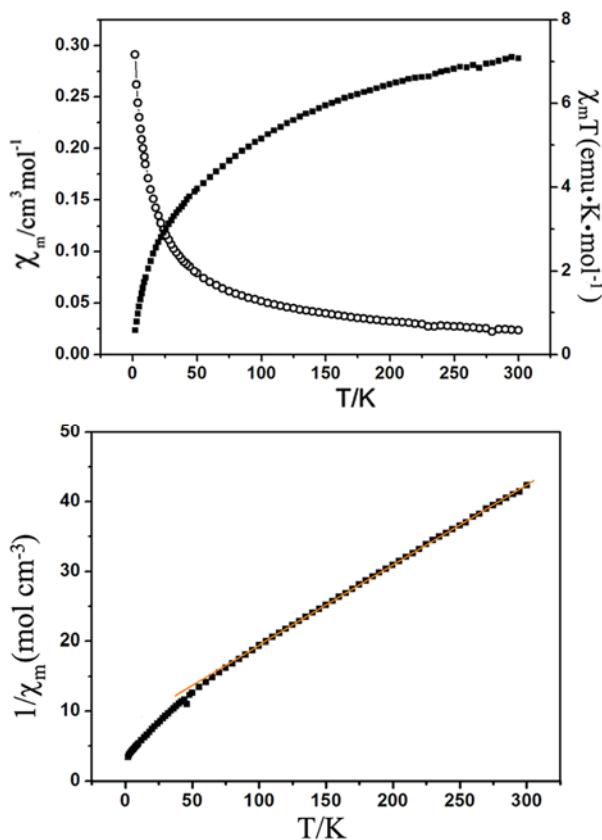
**Figure S19.** The TG curve for 6.



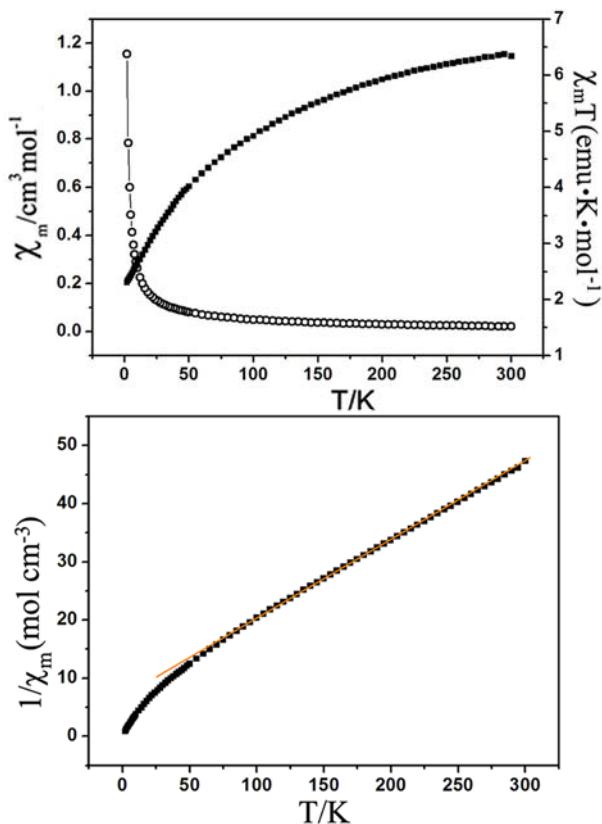
**Figure S20.** The TG curve for 7.



**Figure S21.** The TG curve for 8.



**Figure S22.** Plot of the temperature dependence of  $\chi_m$ ,  $\chi_m T$ , and  $1/\chi_m$  for **3**.



**Figure S23.** Plot of the temperature dependence of  $\chi_m$ ,  $\chi_m T$ , and  $1/\chi_m$  for **4**.

**Table S1** Selected bond distances ( $\text{\AA}$ ) for **1–4**.

Bond	Distance/ $\text{\AA}$			
$\text{Ln}^{\text{III}}$	La	Ce	Pr	Nd
Ln1-O12	2.55(2)	2.514(19)	2.501(16)	2.495(18)
Ln1-O26	2.57(2)	2.551(17)	2.552(17)	2.506(17)
Ln1-O27	2.575(17)	2.575(18)	2.540(15)	2.526(16)
Ln1-O22#2	2.580(18)	2.550(17)	2.535(14)	2.517(18)
Ln1-O21	2.59(3)	2.54(2)	2.53(2)	2.52(2)
Ln1-O14	2.596(19)	2.57(2)	2.544(18)	2.519(18)
Ln1-O33	2.654(18)	2.622(13)	2.581(15)	2.581(19)
Ln1-O29	2.664(18)	2.651(18)	2.595(15)	2.616(16)
Ln1-N1	2.68(2)	2.64(2)	2.621(19)	2.570(13)
Ln1-O48#2	2.945(18)	2.962(16)		
Average Ln1-O	2.639	2.617	2.556	2.538
Ln2-O24	2.506(19)	2.501(17)	2.504(16)	2.467(17)
Ln2-O46	2.51(2)	2.492(17)	2.489(15)	2.472(17)
Ln2-O41#3	2.540(15)	2.496(16)	2.489(16)	2.482(16)
Ln2-O47	2.55(2)	2.53(2)	2.490(18)	2.509(19)
Ln2-O48	2.559(18)	2.516(16)	2.483(14)	2.488(17)
Ln2-O17	2.57(2)	2.55(3)	2.528(18)	2.51(2)
Ln2-O28	2.609(17)	2.593(16)	2.608(16)	2.568(16)
Ln2-N2	2.62(2)	2.601(19)	2.55(2)	2.556(12)
Ln2-O4	2.63(2)	2.587(18)	2.591(18)	2.563(19)
Average Ln2-O	2.566	2.540	2.526	2.513

**Table S2** Selected bond distances ( $\text{\AA}$ ) for **5–8**

Selected bond distances ( $\text{\AA}$ ) for <b>5</b>					
La1-O38	2.435(4)	La2-O40	2.457(5)	La3-O15	2.491(4)
La1-O37#4	2.529(4)	La2-O36#2	2.507(4)	La3-O81	2.492(4)
La1-O80	2.555(4)	La2-O34#3	2.538(4)	La3-O18#1	2.565(4)
La1-O6	2.555(4)	La2-O52	2.548(5)	La3-O12	2.575(4)
La1-O14	2.574(4)	La2-O67	2.559(5)	La3-O53	2.578(4)
La1-O23	2.593(4)	La2-O63	2.576(5)	La3-O48	2.588(4)
La1-O19	2.627(4)	La2-O60	2.612(5)	La3-N2	2.638(4)
La1-O66	2.634(5)	La2-O44	2.671(4)	La3-O41	2.650(4)
La1-O47	2.670(5)	La2-N1	2.675(4)	La3-N3	2.683(4)
				La3-O9	2.837(4)
Average La1-O	2.575(4)	Average La2-O	2.571(5)	Average La3-O	2.610(4)
Selected bond distances ( $\text{\AA}$ ) for <b>6</b>					
Ce1-O11	2.432(14)	Ce2-O52#2	2.445(13)	Ce3-O57	2.460(13)
Ce1-O38	2.530(13)	Ce2-O26	2.478(12)	Ce3-O4	2.461(13)
Ce1-O13	2.534(13)	Ce2-O100#3	2.482(13)	Ce3-O24	2.550(13)
Ce1-O70	2.551(13)	Ce2-O37#4	2.508(12)	Ce3-O7#1	2.554(12)

Ce1-O68	2.568(13)	Ce2-O90	2.560(15)	Ce3-O28	2.564(12)
Ce1-O23	2.569(13)	Ce2-O80	2.563(14)	Ce3-O64	2.575(13)
Ce1-O17	2.584(13)	Ce2-O88	2.568(14)	Ce3-N3	2.603(15)
Ce1-O69	2.613(14)	Ce2-N1	2.616(16)	Ce3-O54	2.626(12)
Ce1-O55	2.622(14)	Ce2-O53	2.628(14)	Ce3-N2	2.638(14)
				Ce3-O9#1	2.986(13)
Average Ce1-O	2.556(13)	Average Ce2-O	2.539(14)	Average Ce3-O	2.602(13)
Selected bond distances (Å) for 7					
Pr1-O10	2.383(15)	Pr2-O52	2.448(14)	Pr3-O60	2.423(14)
Pr1-O51	2.427(15)	Pr2-O33	2.450(12)	Pr3-O14	2.437(13)
Pr1-O46	2.481(15)	Pr2-O62	2.463(14)	Pr3-O43	2.510(14)
Pr1-O17	2.506(13)	Pr2-O24#3	2.464(12)	Pr3-O39	2.542(12)
Pr1-O44	2.521(13)	Pr2-O7	2.510(14)	Pr3-O47#1	2.551(11)
Pr1-O13#3	2.522(13)	Pr2-O48	2.541(16)	Pr3-O42#2	2.552(13)
Pr1-O41	2.535(14)	Pr2-O40	2.554(15)	Pr3-N2	2.572(16)
Pr1-O22	2.553(13)	Pr2-O49	2.639(15)	Pr3-O38	2.637(12)
Pr1-O55	2.615(14)	Pr2-N1	2.647(15)	Pr3-N3	2.639(14)
Average Pr1-O	2.505(14)	Average Pr2-O	2.524(14)	Average Pr3-O	2.540(13)
Selected bond distances (Å) for 8					
Nd1-O(48)	2.411(10)	Nd2-O37	2.412(11)	Nd3-O27	2.417(9)
Nd1-O(16)	2.487(9)	Nd2-O34	2.443(10)	Nd3-O12#1	2.425(10)
Nd1-O(47)	2.491(10)	Nd2-O17#3	2.464(9)	Nd3-O43#2	2.511(9)
Nd1-O(21)	2.500(10)	Nd2-O6	2.481(12)	Nd3-O10#1	2.524(10)
Nd1-O(11)	2.502(10)	Nd2-O64	2.497(10)	Nd3-O46	2.544(9)
Nd1-O(55)	2.526(10)	Nd2-O42	2.499(11)	Nd3-O45	2.553(10)
Nd1-O(7)	2.541(11)	Nd2-O31	2.516(11)	Nd3-N2#1	2.566(12)
Nd1-O(50)	2.545(10)	Nd2-N1	2.612(11)	Nd3-O39	2.586(9)
Nd1-O(53)	2.585(11)	Nd2-O63	2.633(10)	Nd3-N3	2.602(11)
Average Nd1-O	2.510(10)	Average Nd2-O	2.506(11)	Average Nd3-O	2.498(10)