Supporting Information

Anion-Controlled Assembly of a Series of Heterometallic 3d–4f Compounds with 0D Cluster, 1D Chain, 2D Network and 3D Frameworks

Han Zhang, Zhi-Hao Yan, Yun Luo, Xiu-Ying Zheng, Xiang-Jian Kong,* La-Sheng Long,* and Lan-Sun Zheng

Collaborative Innovation Center of Chemistry for Energy Materials, *State Key Laboratory of Physical Chemistry of Solid Surface and Department of Chemistry, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen, 361005, China.*

E-mail: xjkong@xmu.edu.cn, lslong@xmu.edu.cn

Received (in XXX, XXX) Xth XXXXXXXX 2015, Accepted Xth XXXXXXXX 2015



Fig. S1 IR spectrum of 1-7.



Fig. S2 (a) Coordination geometry of the Nd^{3+} ion in 1. (b) The packing of the 0D tetranuclear clusters in the structure of 1.







Fig. S4 (a) Coordination geometry of the La^{3+} ion in 4. (b) The packing of 2D nets of 4.



Fig. S5 (a) Coordination geometry of the La^{3+} ion in 6. (b) The connecting plots of the La_{24} cages in 6.



Fig. S6. The difference of $\chi_M T(\Delta = (\chi_M T)(6) - (\chi_M T)(7))$ between compounds 6 and 7 versus *T*.



Fig. S7 Plots of $\chi_M T$ and χ_M^{-1} versus *T* for compounds 1 (a), 2 (b), 3 (c), 5 (d), 6 (e) and 7(f) over the temperature of range 2-300 K.

complex 1												
Nd1—O1	2.6187 (18)	Nd1—O3	2.5430 (19)	Nd1—O5	2.4748 (19)	Nd1—O6	2.489 (2)					
Nd1-010	2.421 (2)	Nd1—O12 ⁱ	2.4386 (19)	Nd1—O13	2.426 (2)	Nd1—O15	2.527 (2)					
Nd1—017	2.616 (2)	Nd1—N1	3.000 (3)	Ni1—O2	2.0371 (19)	Ni1—O3	2.1009 (19)					
Ni1—O7	2.0197 (19)	Ni1—09	2.0669 (18)	Ni1—N2	2.068 (2)	Ni1—N3	2.098 (2)					
Ni1—O3—Nd1	153.33 (8)											
Symmetry codes: (i): -x+2, -y+2, -z+1												
complex 2												
Dy1—O10	2.345 (4)	Dy1—O8	2.350 (4)	Dy1—O22 ⁱ	2.355 (4)	Dy1-017	2.379 (4)					
Dy1—O1	2.401 (4)	Dy1—O9	2.430 (4)	Dy1—O4	2.458 (4)	Dy1—O7	2.564 (5)					
Dy1—O26	2.572 (4)	Ni1—O24	2.021 (4)	Ni1—012	2.038 (4)	Ni1—036	2.061 (4)					
Ni1—N1	2.071 (5)	Ni1—N2	2.093 (4)	Ni1—O4	2.108 (4)							
Ni1—O4—Dy1	153.78 (18)											
Symmetry codes: (i): 1-x, -1-y, -z												
complex 3												
Dy1-010	2.360 (3)	Dy1—O4	2.289 (3)	Dy1—O7	2.355 (3)	Dy1—O14	2.314 (3)					
Dy1-012	2.372 (3)	Dy1—O11	2.430 (3)	Dy1—O13	2.332 (3)	Dy1—O9	2.367 (3)					
Ni1—O1	2.066 (3)	Ni1—O3	2.028 (3)	Ni1—08	2.037 (3)	Ni1—O5	2.053 (3)					
Ni1—N1	2.060 (3)	Ni1—N2	2.075 (4)									
Symmetry codes: (i) <i>x</i> -1, <i>y</i> -1, <i>z</i> ; (ii) <i>x</i> +1, <i>y</i> +1, <i>z</i> .												
complex 4												
La1—O2 ⁱ	2.497 (3)	La1—O3 ⁱⁱ	2.516 (3)	La1—O5	2.443 (2)	La1—O4W	2.566 (3)					
La1—O5W	2.556 (3)	La1—O6W	2.537 (3)	La1—O7W	2.632 (3)	La1—O8W	2.611 (2)					
La1—O9W	2.548 (3)	Ni1—O1	2.058 (2)	Ni1—O4	2.019 (2)	Ni1—O6	2.019 (2)					
Ni1—O8	2.066 (3)	Ni1—N2	2.079 (3)	Ni1—N1	2.070 (3)							
Symmetry codes:	$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$											
complex 5												
Ni1—O4	2.015 (3)	Ni1—O6	2.020 (3)	Ni1—O2	2.058 (3)	Ni1—N1	2.062 (4)					
Ni1—O8	2.071 (3)	Ni1—N2	2.080 (4)	Nd1—O5	2.401 (3)	Nd1—O1 ⁱ	2.435 (3)					
Nd1—O3ii	2.472 (3)	Nd1—O7W	2.477 (3)	Nd1—O6W	2.479 (3)	Nd1—O8W	2.515 (4)					
Nd1—O4W	2.518 (4)	Nd1—O5W	2.553 (3)	Nd1—O9W	2.576 (3)							
Symmetry codes: (i) <i>x</i> , <i>y</i> +1, <i>z</i> ; (ii) <i>x</i> , - <i>y</i> -1/2, <i>z</i> +1/2;												
complex 6												
Gd1—O1 ⁱ	2.45 (2)	Gd1—O3W	2.50 (2)	Gd1—O1 ⁱⁱ	2.45 (2)	Gd1—O1W ⁱⁱⁱ	2.78 (10)					
Gd1—O1	2.45 (2)	Gd1—O1W	2.78 (10)	Gd1—O1 ⁱⁱⁱ	2.45 (2)	Ni1—O2	1.95 (3)					
Ni1—O2 ^{iv}	1.95 (3)	Ni1—O2 ^v	1.95 (3)	Ni1—O2 ^{vi}	1.95 (3)	Ni1—N1	2.05 (2)					
Symmetry codes:	(i) -x+1, -z, -y	; (ii) <i>x</i> , <i>-z</i> , <i>-y</i> ; (iii)	-x+1, y, z; (iv) y	<i>v, x, z;</i> (v) <i>x, y, −z;</i>	(vi) <i>y</i> , <i>x</i> , − <i>z</i> ;	•						
complex 7												
La1—O1	2.495 (7)	La1—O1 ⁱⁱⁱ	2.495 (7)	La1—O1W	2.582 (9)	La1—O2W	2.609 (9)					
Ni1—N1	2.019 (7)	La1—O1W ⁱ	2.582 (9)	La1—O2W ⁱⁱ	2.609 (9)	Ni1—N1 ^{iv}	2.019 (7)					
La1—O1 ⁱ	2.495 (7)	La1—O1 ⁱⁱ	2.495 (7)									
Symmetry codes: (i) $-x+1$, y, z; (ii) x, $-z$, $-y$; (iii) $-x+1$, $-z$, $-y$; (iv) y, x, $-z$;												

Table. S1: Selected bond lengths and angles (°) for 1 – 7.

<i>D</i> -НА	<i>D</i> -Н	АН	D A	D -НА	
Complex 1					
O1W-H1WAO4	0.87	2.07	2.923(3)	164.3	
$O1W-H1WBO3W^i$	0.87	2.14	2.980(3)	169.1	
O2W-H2WBO2	0.87	2.28	3.001(3)	143.4	
$O3W – H3WA \dots O1W^i$	0.87	2.00	2.826(4)	165.3	
Symmetry codes: (i): $-x+2$, $-y+$	-2, -z+1				
Complex 2					
O1W-H1WAO4	0.87	2.08	2.831(4)	163.5	
$O1W\!-\!H1WB\ldots O3W^i$	0.87	2.34	2.941(4)	170.1	
O2W-H2WBO2	0.87	2.16	3.121(2)	139.2	
$O3W-H3WAO1W^i$	0.87	2.11	2.745(4)	145.9	
Symmetry codes: (i): 1-x, -1-y,	-Z				
Complex 3					
O14W-H14WACl1	0.88	2.48	3.238(3)	144.3	
O10W-H10WACl1	0.88	2.30	3.132(3)	156.5	
O1W-H1WACl1	0.87	2.28	3.140(2)	169.3	
O1W-H1WBCl1 ⁱ	0.87	2.47	3.336(4)	175.1	
Symmetry codes: (i): 1-x, 1-y,	-Z				
Complex 4					
O7W-H7WBO12	0.90	2.07	2.929(5)	158.6	
O7W-H7WBO11	0.90	2.73	3.473(6)	140.0	
Complex 5					
O7W-H7WBO12	0.89	2.11	2.846(3)	159.2	
O7W-H7WBO11	0.89	2.69	3.124(4)	141.3	

Table S2 Hydrogen bond geometries for 1-5.