Electronic Supplementary Information for

The first μ-Ge_2Se_8 ligand to lanthanide(III) centers: solvothermal syntheses and characterizations of lanthanide selenidogermanate complexes with a pentadentate polyamine as a co-ligand

Ruihong Chen, Weiwei Tang, Jingjing Liang, Wenqing Jiang, Yong Zhang and Dingxian Jia*

Key Laboratory of Organic Synthesis of Jiangsu Province, College of Chemistry, Chemical Engineering and Materials Science, Dushu Lake Campus, Soochow University, Suzhou 215123, People's Republic of China.

Table S1. Selected bond lengths (Å) and angles (°) for **1**

Ge(1)–Se(1)	2.297(4)	Ge(1)–Se(2)	2.358(4)
Ge(1)–Se(3)#1	2.351(4)	Ge(1)–Se(4)	2.303(5)
Se(2)–Se(3)	2.287(5)	Eu(1)–Se(1)	3.017(3)
Eu(1)–O(1)	2.282(14)	Eu(1)–O(1)#2	2.356(13)
Eu(1)–N(1)	2.596(19)	Eu(1)–N(2)	2.59(2)
Eu(1)–N(3)	2.61(2)	Eu(1)–N(4)	2.60(2)
Eu(1)–N(5)	2.59(2)	Eu(1)···Eu(1)#2	3.811(2)
Se(1)–Ge(1)–Se(2)	110.32(15)	Se(1)–Ge(1)–Se(3)#1	115.42(16)
Se(1)–Ge(1)–Se(4)	119.95(17)	Se(2)–Ge(1)–Se(3)#1	107.72(16)
Se(2)–Ge(1)–Se(4)	101.45(19)	Se(4)–Ge(1)–Se(3)#1	100.46(17)
Ge(1)–Se(1)–Eu(1)	116.59(11)	Ge(1)–Se(2)–Se(3)	105.55(18)
Ge(1)#1–Se(3)–Se(2)	97.75(16)	Eu(1)–O(1)–Eu(1)#2	110.5(6)
Se(1)–Eu(1)–O(1)	101.3(4)	Se(1)–Eu(1)–O(1)#2	74.2(4)
Se(1)–Eu(1)–N(1)	83.0(5)	Se(1)–Eu(1)–N(2)	86.3(5)
Se(1)–Eu(1)–N(3)	143.9(5)	Se(1)–Eu(1)–N(4)	149.1(4)
Se(1)–Eu(1)–N(5)	84.4(6)	O(1)–Eu(1)–N(1)	149.4(5)
O(1)–Eu(1)–O(1)#2	69.5(6)	O(1)–Eu(1)–N(3)	88.8(6)
O(1)–Eu(1)–N(2)	143.5(5)	O(1)–Eu(1)–N(5)	76.3(7)
O(1)–Eu(1)–N(4)	83.3(6)	O(1)#2–Eu(1)–N(2)	78.7(6)

O(1)#2–Eu(1)–N(1)	139.4(6)	O(1)#2–Eu(1)–N(4)	134.4(5)
O(1)#2–Eu(1)–N(3)	77.3(6)	N(1)–Eu(1)–N(3)	105.6(7)
O(1)#2–Eu(1)–N(5)	134.5(6)	N(1)–Eu(1)–N(5)	73.9(7)
N(1)–Eu(1)–N(2)	66.5(6)	N(2)–Eu(1)–N(4)	108.2(7)
N(1)–Eu(1)–N(4)	78.5(6)	N(3)–Eu(1)–N(4)	65.9(6)
N(2)–Eu(1)–N(3)	66.6(6)	N(4)–Eu(1)–N(5)	66.9(7)
N(2)–Eu(1)–N(5)	140.2(7)	N(3)–Eu(1)–N(5)	131.7(7)
Symmetry transformations used to generate equivalent atoms: #1) –x+1, –y, –z+1; #2) –x+2, –y, –z+1.			

Table S2. Selected bond lengths (Å) and angles (°) for **2**

Ge(1)–Se(1)	2.278(8)	Ge(1)–Se(2)	2.390(10)
Ge(1)–Se(3A)	2.357(12)	Ge(1)–Se(4)	2.265(10)
Ge(1)–Se(3B)	2.45(3)	Ge(1)–Se(3B)#1	2.490(19)
Se(2)–Se(3A)	2.31(2)	Gd(1)–Se(1)	3.002(6)
Gd(1)–O(1)	2.28(4)	Gd(1)–O(1)#2	2.32(3)
Gd(1)–N(1)	2.64(4)	Gd(1)–N(2)	2.56(6)
Gd(1)–N(3)	2.66(3)	Gd(1)–N(4)	2.56(3)
Gd(1)–N(5)	2.59(2)	Gd(1)–Gd(1)#2	3.792(5)
Se(1)–Ge(1)–Se(2)	118.9(4)	Se(1)–Ge(1)–Se(3A)#1	113.4(5)
Se(1)–Ge(1)–Se(4)	119.5(4)	Se(2)–Ge(1)–Se(3A)#1	113.0(5)
Se(2)–Ge(1)–Se(4)	93.3(4)	Se(4)–Ge(1)–Se(3A)#1	95.0(5)
Se(1)–Ge(1)–Se(3B)	104.9(9)	Se(1)–Ge(1)–Se(3B)#1	100.7(9)
Se(4)–Ge(1)–Se(3B)	119.3(8)	Se(4)–Ge(1)–Se(3B)#1	125.5(9)
Ge(1)–Se(1)–Gd(1)	117.7(2)	Ge(1)–Se(2)–Se(3A)	94.5(6)
Ge(1)#1–Se(3A)–Se(2)	98.1(7)	Gd(1)–O(1)–Gd(1)#2	111.3(13)
Ge(1)–Se(3B)–Ge(1)#1	101.2(10)		
Se(1)–Gd(1)–O(1)	74.5(7)	Se(1)–Gd(1)–O(1)#2	101.1(8)
Se(1)–Gd(1)–N(1)	81.6(10)	Se(1)–Gd(1)–N(2)	85.1(10)
Se(1)–Gd(1)–N(3)	144.1(9)	Se(1)–Gd(1)–N(4)	145.3(7)
Se(1)–Gd(1)–N(5)	83.0(8)		
O(1)–Gd(1)–O(1)#2	68.7(13)	O(1)–Gd(1)–N(1)	137.9(12)
O(1)–Gd(1)–N(2)	79.7(13)	O(1)–Gd(1)–N(3)	78.0(11)
O(1)–Gd(1)–N(4)	137.9(12)	O(1)–Gd(1)–N(5)	133.1(12)
O(1)#2–Gd(1)–N(1)	151.2(11)	O(1)#2–Gd(1)–N(2)	144.5(11)
O(1)#2–Gd(1)–N(3)	89.9(10)	O(1)#2–Gd(1)–N(4)	85.5(15)
O(1)#2–Gd(1)–N(5)	76.2(11)		
N(1)–Gd(1)–N(2)	64.0(12)	N(1)–Gd(1)–N(3)	104.8(12)
N(1)–Gd(1)–N(4)	77.3(15)	N(1)–Gd(1)–N(5)	75.7(12)

N(2)–Gd(1)–N(3)	67.5(12)	N(2)–Gd(1)–N(4)	109.2(16)
N(2)–Gd(1)–N(5)	139.2(12)	N(3)–Gd(1)–N(4)	68.9(11)
N(3)–Gd(1)–N(5)	132.9(12)	N(4)–Gd(1)–N(5)	65.4(8)
Symmetry transformations used to generate equivalent atoms: #1 –x, –y+1, –z+1; #2 –x+1, –y+1, –z+1			

Table S3. Selected bond lengths (Å) and angles (°) for **3**

Ge(1)–Se(1)	2.292(3)	Ge(1)–Se(2)	2.361(4)
Ge(1)–Se(3)#1	2.351(4)	Ge(1)–Se(4)	2.315(4)
Se(2)–Se(3)	2.313(5)	Dy(1)–Se(1)	2.979(2)
Dy(1)–O(1)	2.247(13)	Dy(1)–O(1)#2	2.291(15)
Dy(1)–N(1)	2.53(2)	Dy(1)–N(2)	2.529(19)
Dy(1)–N(3)	2.566(17)	Dy(1)–N(4)	2.557(17)
Dy(1)–N(5)	2.542(17)	Dy(1)···Dy(1)#2	3.747(2)
Se(1)–Ge(1)–Se(2)	110.66(14)	Se(1)–Ge(1)–Se(3)#1	115.68(15)
Se(1)–Ge(1)–Se(4)	119.85(16)	Se(2)–Ge(1)–Se(3)#1	107.42(15)
Se(2)–Ge(1)–Se(4)	100.90(17)	Se(4)–Ge(1)–Se(3)#1	100.68(16)
Ge(1)–Se(1)–Dy(1)	117.40(11)	Ge(1)–Se(2)–Se(3)	105.44(16)
Ge(1)#1–Se(3)–Se(2)	97.74(15)	Dy(1)–O(1)–Dy(1)#2	111.3(6)
Se(1)–Dy(1)–O(1)	73.3(4)	Se(1)–Dy(1)–O(1)#2	101.6(4)
Se(1)–Dy(1)–N(1)	83.7(5)	Se(1)–Dy(1)–N(2)	149.2(5)
Se(1)–Dy(1)–N(3)	143.3(4)	Se(1)–Dy(1)–N(4)	85.1(5)
Se(1)–Dy(1)–N(5)	82.8(5)		
O(1)–Dy(1)–O(1)#2	68.7(6)	O(1)–Dy(1)–N(1)	132.6(6)
O(1)–Dy(1)–N(2)	135.0(6)	O(1)–Dy(1)–N(3)	77.8(5)
O(1)–Dy(1)–N(4)	79.3(5)	O(1)–Dy(1)–N(5)	140.1(5)
O(1)#2–Dy(1)–N(1)	76.6(6)	O(1)#2–Dy(1)–N(2)	83.3(5)
O(1)#2–Dy(1)–N(3)	88.1(5)	O(1)#2–Dy(1)–N(4)	143.4(5)
O(1)#2–Dy(1)–N(5)	149.1(6)		
N(1)–Dy(1)–N(2)	67.8(7)	N(1)–Dy(1)–N(3)	133.0(6)
N(1)–Dy(1)–N(4)	140.0(6)	N(1)–Dy(1)–N(5)	73.5(6)
N(2)–Dy(1)–N(3)	66.4(6)	N(2)–Dy(1)–N(4)	109.1(6)
N(2)–Dy(1)–N(5)	78.4(6)	N(3)–Dy(1)–N(4)	67.6(6)
N(3)–Dy(1)–N(5)	106.7(6)	N(4)–Dy(1)–N(5)	67.0(6)
Symmetry transformations used to generate equivalent atoms: #1) –x+1, –y, –z; #2) –x, –y, –z.			

Table S4. Selected bond lengths (Å) and angles (°) for **4**

Ge(1)–Se(1)	2.4239(12)	Ge(1)–Se(1)#1	2.4139(12)
Ge(1)–Se(2)	2.2921(12)	Ge(1)–Se(3)	2.3048(12)
Dy(1)–Dy(1)#2	3.7472(8)		
Dy(1)–O(1)	2.235(5)	Dy(1)–O(1)#2	2.268(5)
Dy(1)–N(1)	2.510(7)	Dy(1)–N(2)	2.535(7)
Dy(1)–N(3)	2.550(7)	Dy(1)–N(4)	2.473(7)
Dy(1)–N(5)	2.482(6)	Dy(1)–N(6)	2.571(6)
Se(1)#1–Ge(1)–Se(1)	92.57(4)	Se(2)–Ge(1)–Se(1)	114.01(5)
Se(2)–Ge(1)–Se(1)#1	110.96(5)	Se(3)–Ge(1)–Se(1)	113.49(5)
Se(3)–Ge(1)–Se(1)#1	114.53(4)	Se(3)–Ge(1)–Se(2)	110.33(5)
Ge(1)#1–Se(1)–Ge(1)	87.43(4)	Dy(1)–O(1)–Dy(1)#2	112.6(2)
O(1)–Dy(1)–O(1)#2	67.4(2)	O(1)–Dy(1)–N(1)	98.4(2)
O(1)–Dy(1)–N(2)	80.3(2)	O(1)–Dy(1)–N(3)	78.9(2)
O(1)–Dy(1)–N(4)	100.9(2)	O(1)–Dy(1)–N(5)	151.9(2)
O(1)–Dy(1)–N(6)	141.5(2)	O(1)#2–Dy(1)–N(1)	88.2(2)
O(1)#2–Dy(1)–N(2)	135.8(2)	O(1)#2–Dy(1)–N(3)	127.3(2)
O(1)#2–Dy(1)–N(4)	80.5(2)	O(1)#2–Dy(1)–N(5)	139.6(2)
O(1)#2–Dy(1)–N(6)	74.7(2)	N(1)–Dy(1)–N(2)	66.9(2)
N(1)–Dy(1)–N(3)	137.5(2)	N(1)–Dy(1)–N(4)	151.7(2)
N(1)–Dy(1)–N(5)	91.3(2)	N(1)–Dy(1)–N(6)	73.4(2)
N(2)–Dy(1)–N(3)	70.9(2)	N(2)–Dy(1)–N(4)	136.8(2)
N(2)–Dy(1)–N(5)	79.4(2)	N(2)–Dy(1)–N(6)	126.3(2)
N(3)–Dy(1)–N(4)	67.2(2)	N(3)–Dy(1)–N(5)	76.2(2)
N(3)–Dy(1)–N(6)	132.5(2)	N(4)–Dy(1)–N(5)	81.2(2)
N(6)–Dy(1)–N(4)	78.5(2)	N(6)–Dy(1)–N(5)	66.5(2)
Symmetry transformations used to generate equivalent atoms: #1) –x+2, –y+1, –z+1; #2) –x+1, –y+2, –z+1.			

Table S5. Hydrogen Bond lengths (Å) and angles (°) for **1**–**4**

D–H···A	d(H···A)	d(D···A)	<(DHA)
1			
O(1)–H(1)···Se(4)#1	2.69	3.599(14)	166.7
N(1)–H(1A)···Se(4)	2.76	3.65(2)	172.2
N(1)–H(1B)···Se(1)#2	3.03	3.72(2)	135.1
N(2)–H(2)···Se(4)#3	2.69	3.60(2)	176.7
N(3)–H(3)···Se(1)#4	2.83	3.68(2)	156.4
N(4)–H(4)···Se(2)#2	2.62	3.45(2)	151.1
2			
O(1)–H(1)···Se(4)#1	2.85	3.76(3)	164.9
N(1)–H(1A)···Se(1)#2	2.95	3.69(3)	139.0
N(2)–H(2)···Se(4)#1	2.68	3.59(5)	168.0
N(3)–H(3)···Se(1)#3	2.85	3.72(3)	159.2
N(4)–H(4)···Se(2A)#2	2.52	3.36(4)	152.2
N(5)–H(5B)···Se(3A)	2.87	3.56(5)	133.7
3			
O(1)–H(1)···Se(4)#1	2.66	3.588(14)	169.2
N(1)–H(1A)···Se(3)#2	3.03	3.76(2)	137.7
N(2)–H(2)···Se(2)#3	2.62	3.460(17)	150.8
N(3)–H(3)···Se(1)#4	2.77	3.624(18)	156.0
N(4)–H(4)···Se(4)#1	2.69	3.60(2)	176.8
N(5)–H(5B)···Se(1)#1	3.08	3.748(19)	132.2
4			
O(1)–H(1)···Se(2)	3.02	3.673(6)	128.3
N(2)–H(2B)···Se(3)#1	2.75	3.595(7)	156.4
N(4)–H(4A)···Se(2)#2	2.69	3.468(7)	145.6
N(4)–H(4B)···Se(2)#3	2.73	3.592(7)	161.9
N(5)–H(5A)···Se(3)#1	2.62	3.508(7)	169.5
N(6)–H(6B)···Se(3)#4	2.86	3.648(7)	146.9

Symmetry transformations used to generate equivalent atoms: For **1**: #1) x+1/2, –y+1/2, z+1/2; #2) –x+3/2, y+1/2, –z+1/2; #3) –x+3/2, y–1/2, –z+1/2; #4) –x+2, –y, –z+1. For **2**: #1) –x+1/2, y+1/2, –z+1/2; #2) –x+1/2, y–1/2, –z+1/2; #3) –x+1, –y+1, –z+1. For **3**: #1) –x+1/2, y–1/2, –z+1/2; #2) –x+1, –y, –z; #3) –x+1/2, y+1/2, –z+1/2; #4) –x, –y, –z. For **4**: #1) –x+1, –y+1, –z+1; #2) –x+1, –y+2, –z+1; #3) x–1, y, z; #4) x–1/2, –y+3/2, z–1/2.

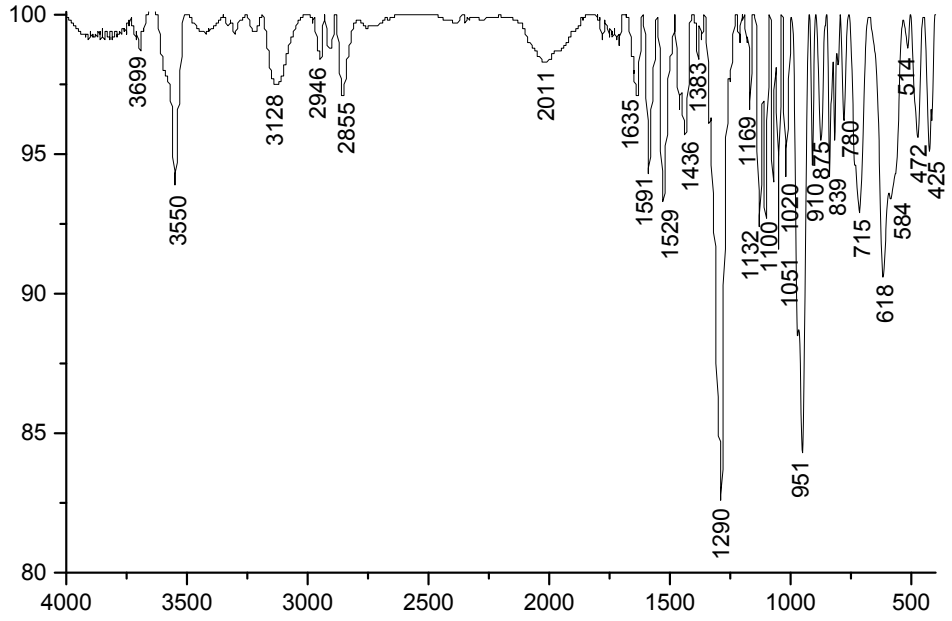

Fig. S-IR1. IR spectrum of complex **1**.

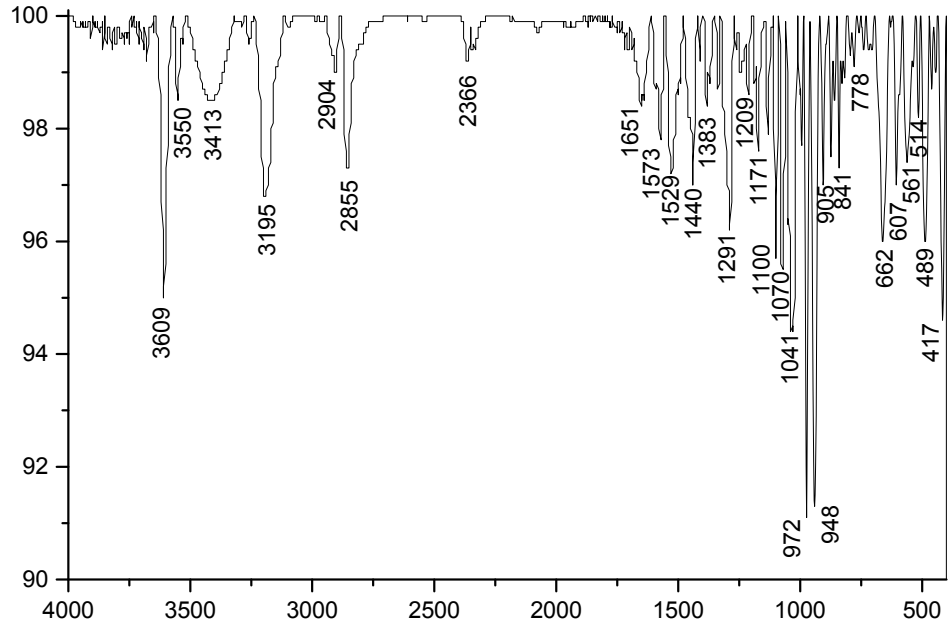

Fig. S-IR2. IR spectrum of complex **2**.

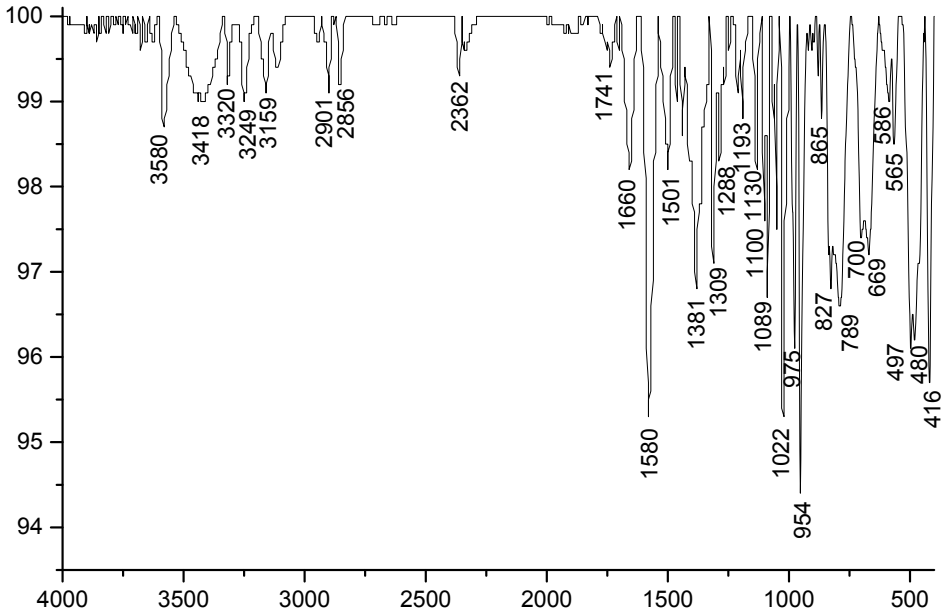

Fig. S-IR3. IR spectrum of complex **3**.

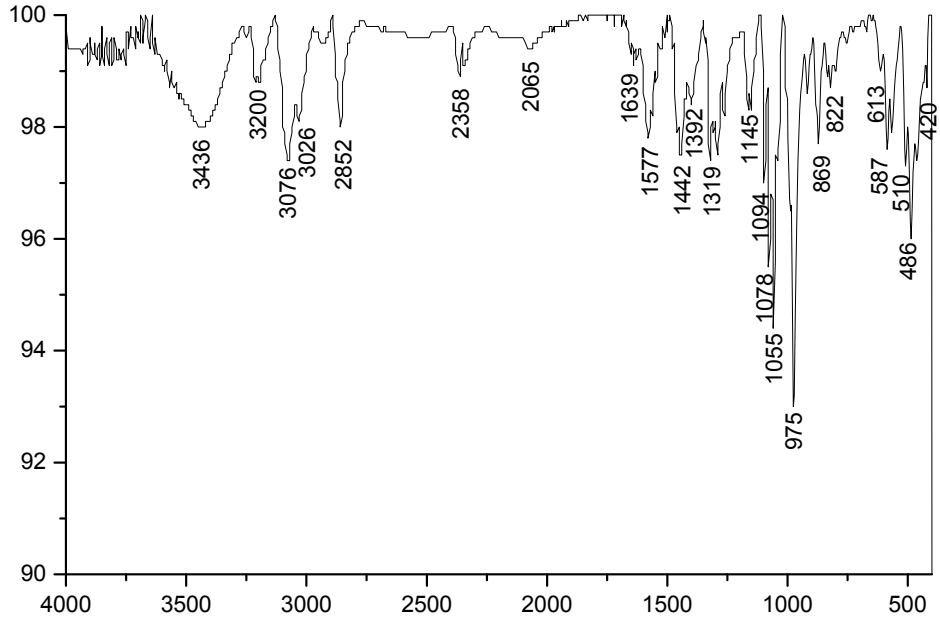

Fig. S-IR4. IR spectrum of complex **4**.

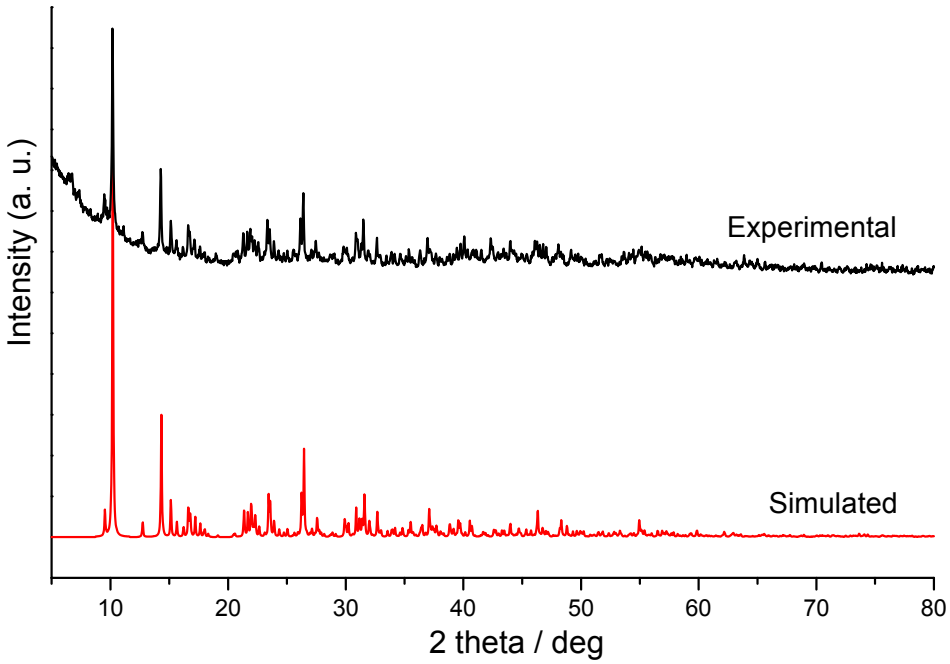

Fig. S1. Powder X-Ray diffraction pattern (black) of the polycrystalline sample of compound **1** and the simulated pattern (red) base on the single crystal data.

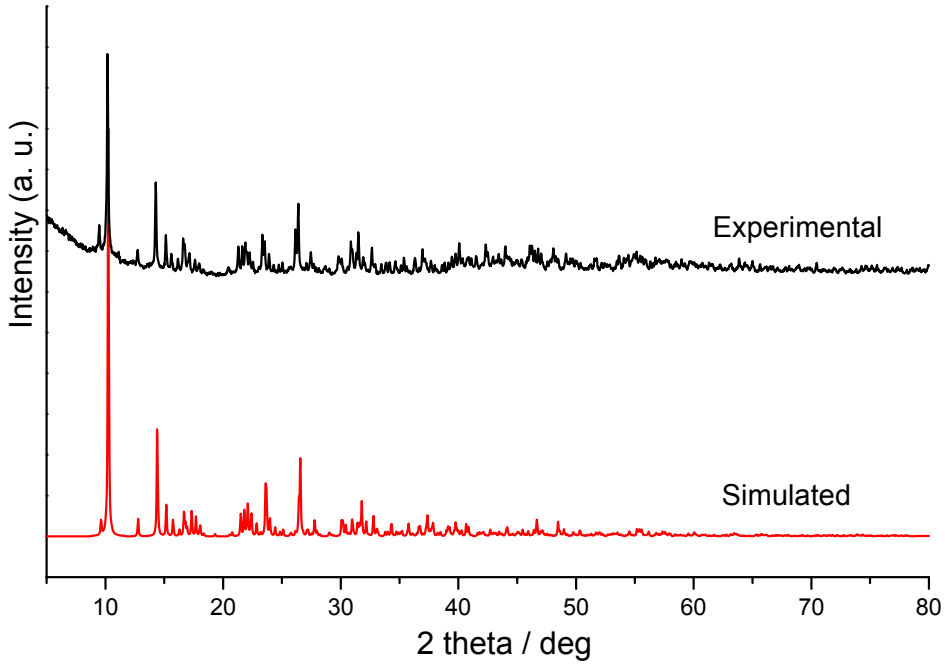

Fig. S2. Powder X-Ray diffraction pattern (black) of the polycrystalline sample of compound **2** and the simulated pattern (red) base on the single crystal data.

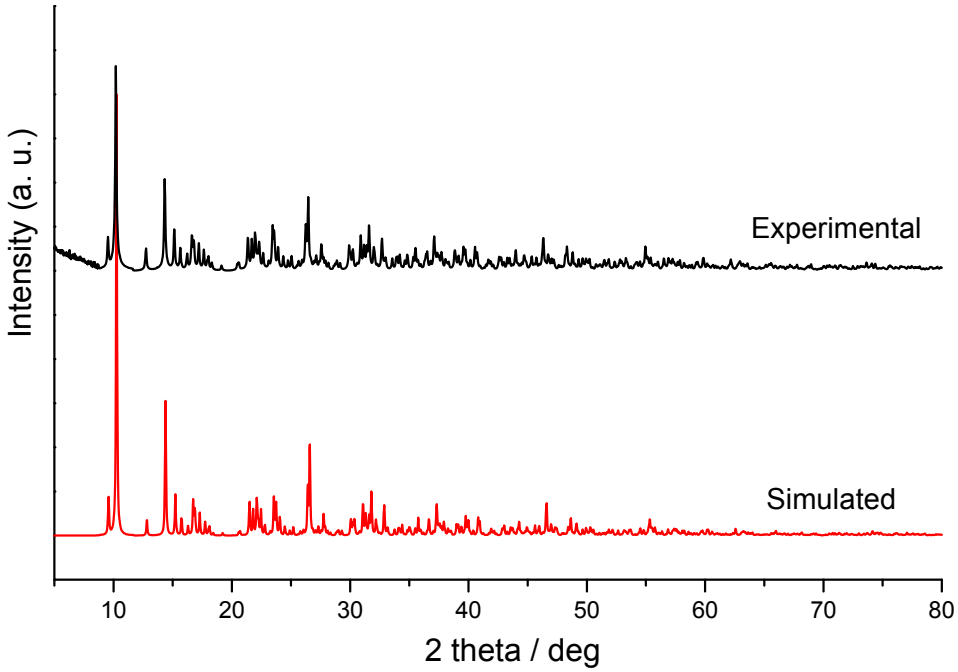

Fig. S3. Powder X-Ray diffraction pattern (black) of the polycrystalline sample of compound **3** and the simulated pattern (red) base on the single crystal data.

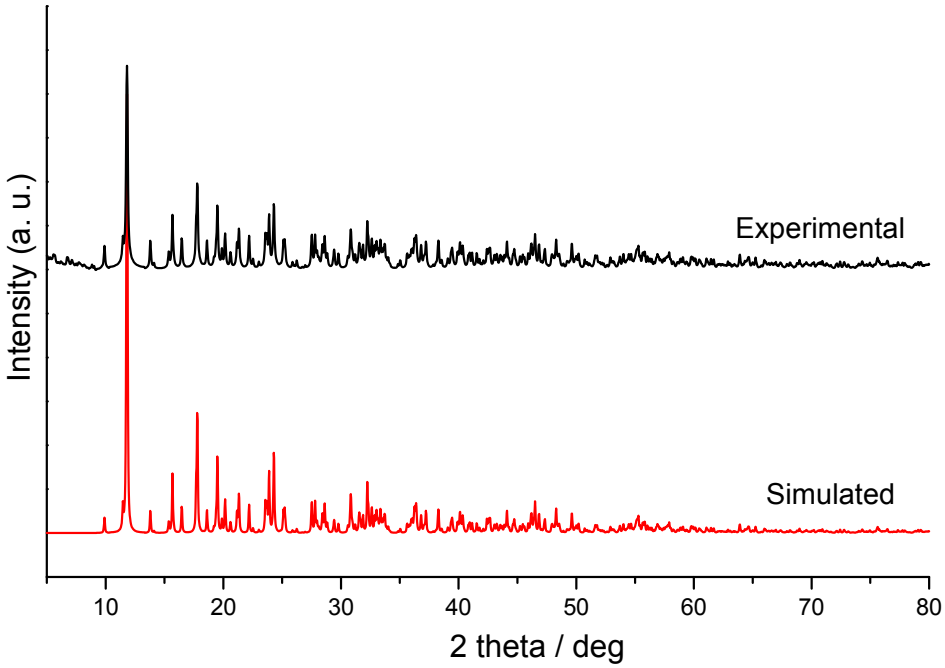

Fig. S4. Powder X-Ray diffraction pattern (black) of the polycrystalline sample of compound **4** and the simulated pattern (red) base on the single crystal data.

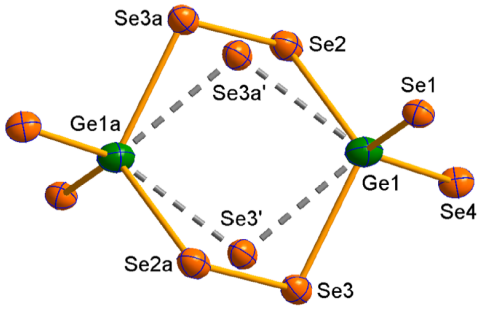

Fig. S5. Crystal structures of $[Ge_2Se_8]^{4-}$ fragment in **2**, showing atom labels (thermal ellipsoids are shown at 50% probability).

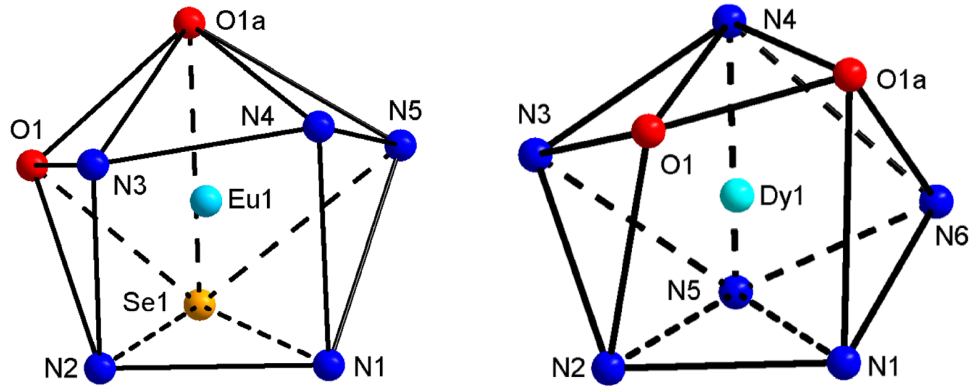

Fig. S6. The bicapped trigonal prisms of EuN_5O_2Se (left) in **1** and DyN_6O_2 (right) in **4**

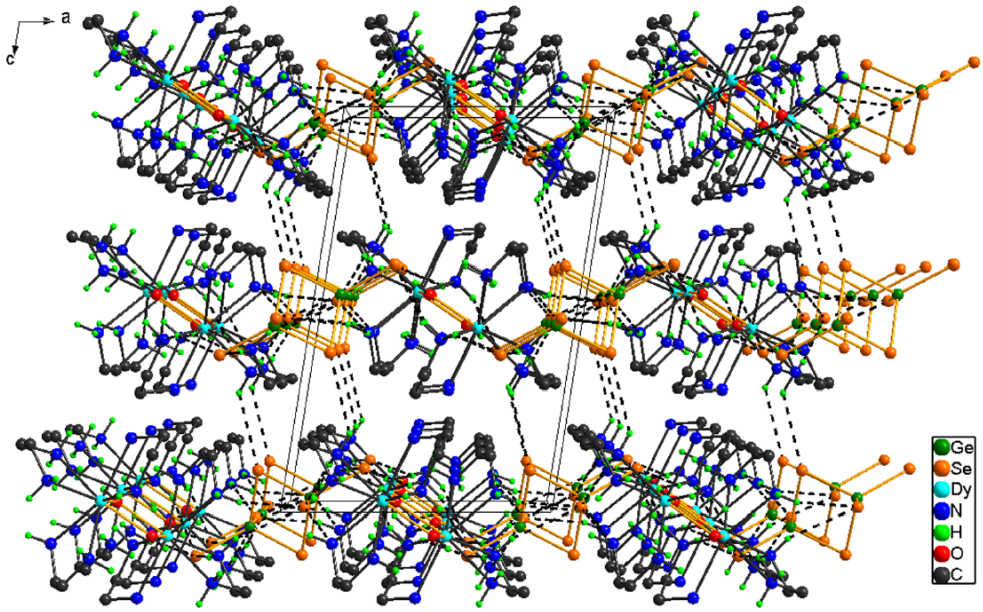

Fig. S7. Crystal packing diagram of **4** viewed along *b* axis. Hydrogen atoms of C–H are omitted for clarity.