Supporting Information

Solvothermal Syntheses, Crystal Structures, and Characterization of a Series of One-Dimensional Organic-containing Gallium Polyselenides

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Supporting Information

Table S1. Selected bond lengths (Å) and angles (°) for compounds **1**-**5**[a].

	$[1,3\text{-pdaH}_2][Ga_2Se_2(Se_2)(Se_3)]$ (**1**)		
Ga(2)-Se(2)	2.3880(12)	Ga(2)-Se(1)#1	2.3991(12)
Ga(2)-Se(4)	2.4105(12)	Ga(2)-Se(7)#1	2.4291(13)
Ga(1)-Se(2)	2.3772(12)	Ga(1)-Se(1)	2.3908(12)
Ga(1)-Se(3)	2.4077(12)	Ga(1)-Se(5)	2.4295(11)
Se(1)-Ga(2)#2	2.3991(12)	Se(4)-Se(3)	2.3621(12)
Se(5)-Se(6)	2.3486(13)	Se(6)-Se(7)	2.3415(13)
Se(7)-Ga(2)#2	2.4291(13)		
Se(2)-Ga(2)-Se(1)#1	108.43(5)	Se(2)-Ga(2)-Se(4)	110.74(5)
Se(1)#1-Ga(2)-Se(4)	111.44(5)	Se(2)-Ga(2)-Se(7)#1	105.30(4)
Se(1)#1-Ga(2)-Se(7)#1	110.19(5)	Se(4)-Ga(2)-Se(7)#1	110.56(5)
Se(2)-Ga(1)-Se(1)	110.12(5)	Se(2)-Ga(1)-Se(3)	107.97(4)
Se(1)-Ga(1)-Se(3)	108.11(5)	Se(2)-Ga(1)-Se(5)	113.97(5)
Se(1)-Ga(1)-Se(5)	111.53(4)	Se(3)-Ga(1)-Se(5)	104.79(4)
Ga(1)-Se(1)-Ga(2)#2	98.42(4)	Ga(1)-Se(2)-Ga(2)	96.82(4)
Se(3)-Se(4)-Ga(2)	99.51(4)	Se(4)-Se(3)-Ga(1)	95.32(4)
Se(6)-Se(5)-Ga(1)	97.71(4)	Se(7)-Se(6)-Se(5)	104.61(5)
Se(6)-Se(7)-Ga(2)#2	96.45(4)		
	$[1,4\text{-bdaH}_2][Ga_2Se_3(Se_2)]$ (**2**)		
Ga(1)-Se(1)	2.3969(5)	Ga(1)-Se(3)#1	2.4014(5)
Ga(1)-Se(2)	2.4221(5)	Ga(1)-Se(3)	2.4268(5)
Se(1)-Ga(1)#2	2.3969(5)	Se(2)-Se(2)#2	2.3712(6)
Se(3)-Ga(1)#1	2.4014(5)		
Se(1)-Ga(1)-Se(3)#1	115.399(19)	Se(1)-Ga(1)-Se(2)	108.078(17)
Se(3)#1-Ga(1)-Se(2)	109.831(18)	Se(1)-Ga(1)-Se(3)	109.389(16)
Se(3)#1-Ga(1)-Se(3)	100.515(16)	Se(2)-Ga(1)-Se(3)	113.656(19)
Ga(1)-Se(1)-Ga(1)#2	95.36(2)	Se(2)#2-Se(2)-Ga(1)	92.876(14)
Ga(1)#1-Se(3)-Ga(1)	79.485(16)		
	$[Me_2NH]_2[Ga_2Se_2(Se_2)_2]$ (**3**)		
Ga(1)-Se(2)	2.385(2)	Ga(1)-Se(1)	2.3946(19)
Ga(1)-Se(6)#1	2.409(2)	Ga(1)-Se(3)	2.418(2)
Ga(2)-Se(1)	2.378(2)	Ga(2)-Se(2)#2	2.4085(19)

Ga(2)-Se(4)	2.422(2)	Ga(2)-Se(5)	2.4301(19)
Se(2)-Ga(2)#1	2.4085(19)	Se(3)-Se(4)	2.364(2)
Se(5)-Se(6)	2.357(2)	Se(6)-Ga(1)#2	2.409(2)
Se(2)-Ga(1)-Se(1)	112.45(6)	Se(2)-Ga(1)-Se(6)#1	110.98(7)
Se(1)-Ga(1)-Se(6)#1	109.76(5)	Se(2)-Ga(1)-Se(3)	105.92(6)
Se(1)-Ga(1)-Se(3)	107.01(8)	Se(6)#1-Ga(1)-Se(3)	110.60(5)
Se(1)-Ga(2)-Se(2)#2	113.21(7)	Se(1)-Ga(2)-Se(4)	111.71(5)
Se(2)#2-Ga(2)-Se(4)	111.67(5)	Se(1)-Ga(2)-Se(5)	108.92(6)
Se(2)#2-Ga(2)-Se(5)	105.04(7)	Se(4)-Ga(2)-Se(5)	105.76(7)
Ga(2)-Se(1)-Ga(1)	98.40(7)	Ga(1)-Se(2)-Ga(2)#1	95.14(8)
Se(4)-Se(3)-Ga(1)	98.60(7)	Se(3)-Se(4)-Ga(2)	99.71(5)
Se(6)-Se(5)-Ga(2)	92.82(7)	Se(5)-Se(6)-Ga(1)#2	97.82(5)
	α-[AEPH]$_2$[Ga$_2$Se$_2$(Se$_2$)$_2$] (**4**)		
Ga(1)-Se(4)#1	2.3822(13)	Ga(1)-Se(1)	2.3854(12)
Ga(1)-Se(2)	2.4241(14)	Ga(1)-Se(6)#1	2.4413(12)
Ga(2)-Se(4)	2.3767(12)	Ga(2)-Se(1)	2.3905(13)
Ga(2)-Se(3)	2.4079(12)	Ga(2)-Se(5)	2.4385(13)
Se(2)-Se(3)	2.3624(13)	Se(4)-Ga(1)#2	2.3822(13)
Se(5)-Se(6)	2.3626(12)	Se(6)-Ga(1)#2	2.4413(12)
Se(4)#1-Ga(1)-Se(1)	115.53(5)	Se(4)#1-Ga(1)-Se(2)	111.25(5)
Se(1)-Ga(1)-Se(2)	110.28(5)	Se(4)#1-Ga(1)-Se(6)#1	104.92(5)
Se(1)-Ga(1)-Se(6)#1	108.06(4)	Se(2)-Ga(1)-Se(6)#1	106.21(5)
Se(4)-Ga(2)-Se(1)	111.08(5)	Se(4)-Ga(2)-Se(3)	111.45(5)
Se(1)-Ga(2)-Se(3)	106.18(5)	Se(4)-Ga(2)-Se(5)	110.18(5)
Se(1)-Ga(2)-Se(5)	111.41(5)	Se(3)-Ga(2)-Se(5)	106.39(5)
Ga(1)-Se(1)-Ga(2)	96.55(5)	Se(3)-Se(2)-Ga(1)	94.59(5)
Se(2)-Se(3)-Ga(2)	95.16(4)	Ga(2)-Se(4)-Ga(1)#2	94.98(5)
Se(6)-Se(5)-Ga(2)	93.54(5)	Se(5)-Se(6)-Ga(1)#2	91.29(4)
	β-[AEPH][GaSe(Se$_2$)] (**5**)		
Ga(1)-Se(3)	2.3717(13)	Ga(1)-Se(3)#1	2.3849(12)
Ga(1)-Se(2)	2.4206(13)	Ga(1)-Se(1)#2	2.4350(13)
Se(1)-Se(2)	2.3517(13)	Se(1)-Ga(1)#1	2.4350(13)
Se(3)-Ga(1)#2	2.3849(12)		
Se(3)-Ga(1)-Se(3)#1	109.83(5)	Se(3)-Ga(1)-Se(2)	110.70(4)
Se(3)#1-Ga(1)-Se(2)	104.06(4)	Se(3)-Ga(1)-Se(1)#2	109.80(4)
Se(3)#1-Ga(1)-Se(1)#2	115.78(5)	Se(2)-Ga(1)-Se(1)#2	106.46(5)
Se(2)-Se(1)-Ga(1)#1	98.57(4)	Se(1)-Se(2)-Ga(1)	96.30(5)
Ga(1)-Se(3)-Ga(1)#2	98.57(5)		

[a] Symmetry transformations used to generate equivalent atoms: For **1**: #1 -*x*+1, *y*-1/2, -*z*+1; #2 -*x*+1, *y*+1/2, -*z*+1; For **2**: #1 -*x*+3/2, -*y*+3/2, -*z*+2; #2 -*x*+1, *y*, -*z*+3/2; For **3**: #1 *x*, -*y*+3/2, *z*-1/2; #2 *x*, -*y*+3/2, *z*+1/2; For **4**: #1 *x*+1, *y*, *z*; #2 *x*-1, *y*, *z*; For **5**: #1 *x*, -*y*+3/2, *z*+1/2; #2 *x*, -*y*+3/2, *z*-1/2.

Table S2. Hydrogen bonds for [1,3-pdaH$_2$][Ga$_2$Se$_7$] **(1)**

D–H···A	d(D–H) (Å)	d(H···A) (Å)	d(D···A) (Å)	<(DHA) (^{o})
N(1)-H(1B)...Se(3)	0.89	2.88	3.442(8)	122.9
C(2)-H(2E)...Se(2)	0.97	2.97	3.819(9)	146.8
N(1)-H(1A)...Se(2)#3	0.89	2.53	3.311(8)	146.5
N(2)-H(2A)...Se(5)#2	0.89	2.69	3.552(8)	162.4
N(2)-H(2C)...Se(1)#4	0.89	2.66	3.534(8)	166.0

Symmetry codes: #2 -*x*+1, *y*+1/2, -*z*+1; #3 *x*+1, *y*, *z*; #4 *x*, *y*, *z*-1.

Table S3. Hydrogen bonds for $[1,4\text{-bda}H_2][Ga_2Se_5]$ **(2)**

D–H···A	d(D–H) (Å)	d(H···A) (Å)	d(D···A) (Å)	<(DHA) (°)
N(1)-H(1D)...Se(1)	0.89	2.60	3.401(3)	150.6
N(1)-H(1E)...Se(2)#4	0.89	2.75	3.390(3)	130.1
N(1)-H(1C)...Se(3)#4	0.89	2.47	3.357(3)	176.9

Symmetry codes: #4 -*x*+3/2,*y*-1/2,-*z*+3/2

Table S4. Hydrogen bonds for $[Me_2NH_2]_2[Ga_2Se_6]$ **(3)**

D–H···A	d(D–H) (Å)	d(H···A) (Å)	d(D···A) (Å)	<(DHA) (°)
N(1)-H(1A)...Se(3)	0.90	2.60	3.473(9)	163.2
N(2A)-H(2E)...Se(2)	0.90	2.64	3.506(12)	162.7
N(1)-H(1B)...Se(5)#3	0.90	2.61	3.456(9)	157.7
N(2A)-H(2D)...Se(1)#4	0.90	2.88	3.609(13)	139.3

Symmetry codes: #3 -*x*+1, *y*-1/2, -*z*+3/2; #4 -*x*, -*y*+1, -*z*+1.

Table S5. Hydrogen bonds for α-$[AEPH]_2[Ga_2Se_6]$ **(4)**

D–H···A	d(D–H) (Å)	d(H···A) (Å)	d(D···A) (Å)	<(DHA) (°)
N(1)-H(1A)...Se(1)	0.86	2.76	3.614(7)	173.8
N(1)-H(1B)...N(3)#3	0.86	1.81	2.653(10)	165.0
N(3)-H(3A)...Se(3)#4	0.86	2.76	3.528(9)	148.7
N(4)-H(4A)...N(6)#5	0.90	1.82	2.723(9)	176.9
N(6)-H(6A)...Se(5)#6	0.89	2.63	3.508(7)	171.2
N(6)-H(6B)...Se(6)#7	0.89	2.58	3.429(8)	160.5

Symmetry codes: #3 *x*+1/2, -*y*+2, *z*+1/2 ; #4 *x*, *y*, *z*-1; #5 *x*+1/2, -*y*+1, *z*+1/2; #6 *x*-1/2, -*y*+1, *z*-1/2; #7 *x*+1/2, -*y*+1, *z*-1/2.

Table S6. Hydrogen bonds for β-$[AEPH][GaSe_3]$ **(5)**

D–H···A	d(D–H) (Å)	d(H···A) (Å)	d(D···A) (Å)	<(DHA) (°)
N(1)-H(1E)...Se(2)#3	0.89	2.64	3.511(6)	165.8
N(1)-H(1B)...N(1)#3	0.89	1.79	2.674(14)	170.4
N(2)-H(2A)...N(2)#4	0.90	1.83	2.729(12)	173.8
C(5)-H(5B)...Se(3)#4	0.97	2.96	3.704(7)	134.0

Symmetry codes: #3 -*x*+1, -*y*+1, -*z*+1 ; #4 -*x*, -*y*+1, -*z*.

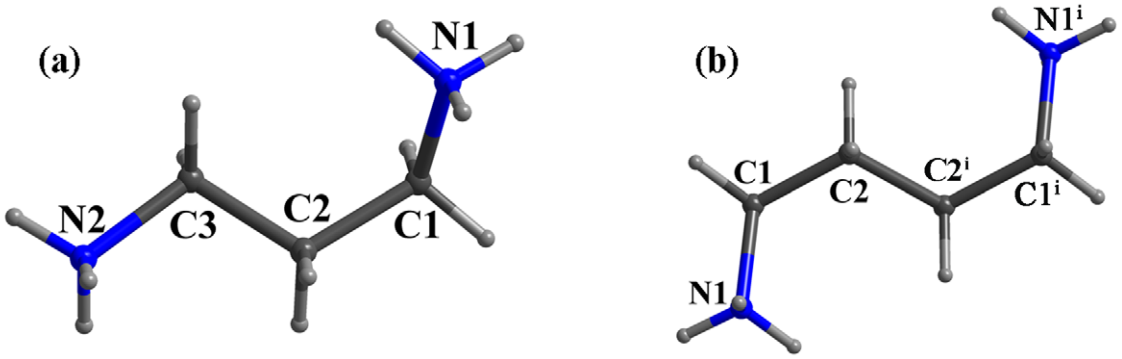

Figure S1. (a) The 1,3-diaminopropane cation in compound **1** have TG conformation (mixture of *trans* (*T*)and *gauche* (*G*)); (b) The 1,4-diaminobutane cation in compound **2** take GTG conformation.

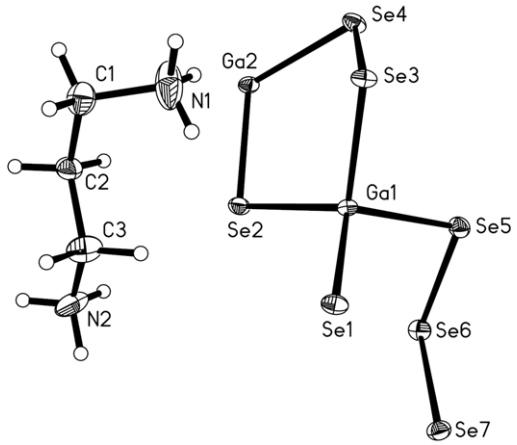

Figure S2. *ORTEP* plot showing the crystallographically asymmetric unit in **1**; thermal ellipsoids are given at the 30% probability level.

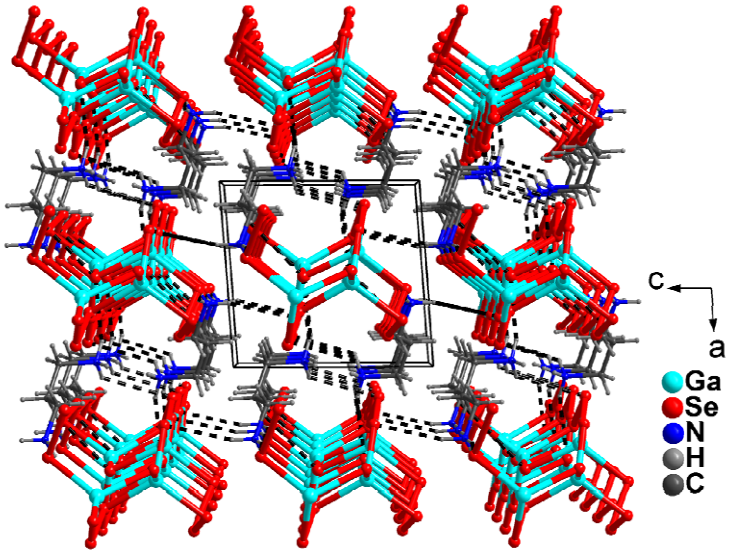

Figure S3. Perspective view of the structure of compound **1** along the *b*-axis; N–H···Se and C–H···Se hydrogen bonds are drawn in dotted lines.

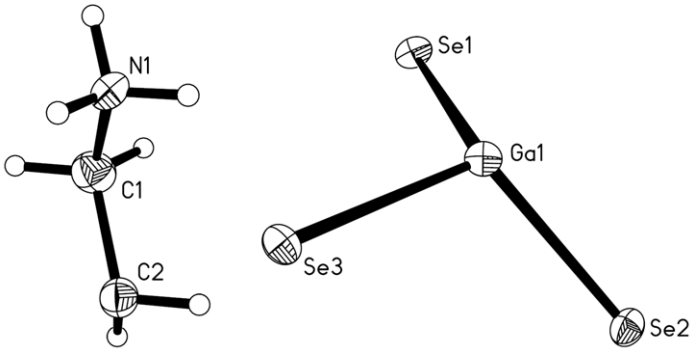

Figure S4. *ORTEP* plot showing the crystallographically asymmetric unit in **2**; thermal ellipsoids are given at the 30% probability level.

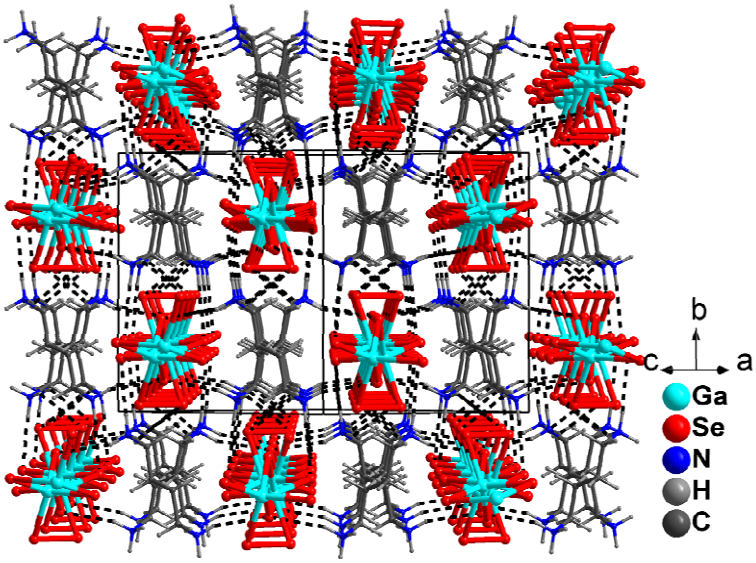

Figure S5. Perspective view of the structure of compound **2** along [101]; N–H···Se hydrogen bonds are drawn in dotted lines.

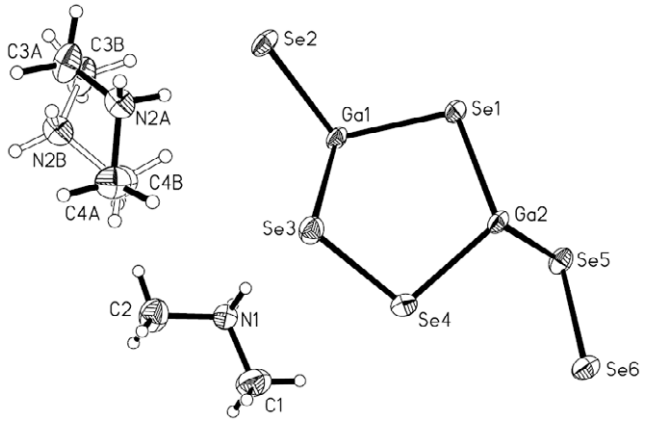

Figure S6. *ORTEP* plot showing the crystallographically asymmetric unit in **3**; thermal ellipsoids are given at the 30% probability level.

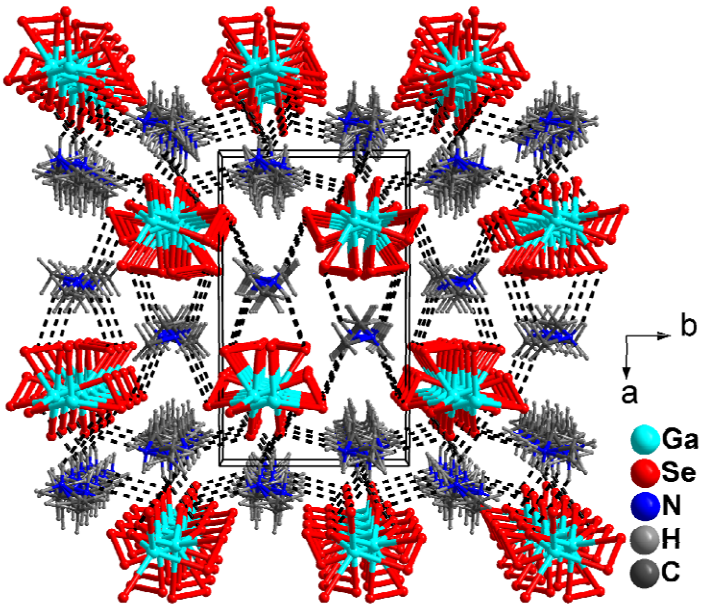

Figure S7. Perspective view of the structure of compound **3** along the *c*-axis; N–H···Se hydrogen bonds are drawn in black dotted lines.

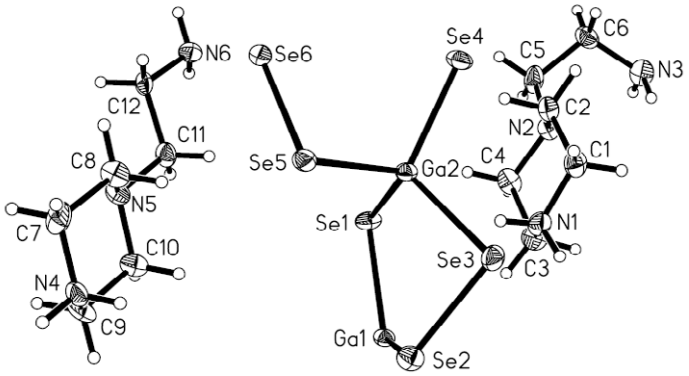

Figure S8. *ORTEP* plot showing the crystallographically asymmetric unit in **4**; thermal ellipsoids are given at the 30% probability level.

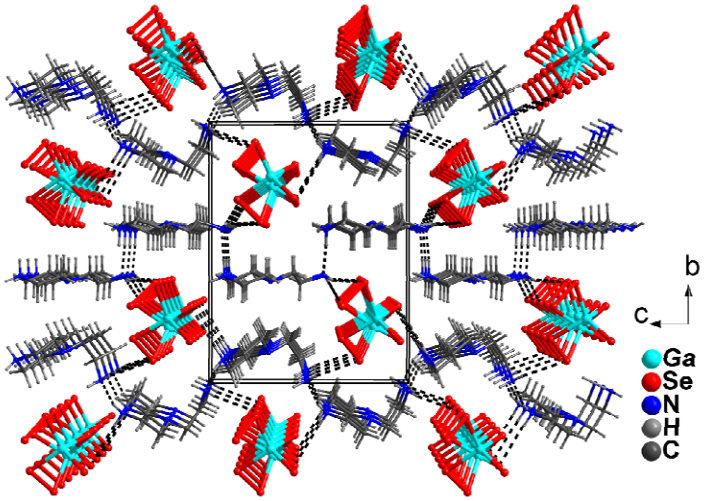

Figure S9. Perspective view of the structure of compound **4** along the *a*-axis; N–H···Se and N–H···N hydrogen bonds are drawn in black dotted lines.

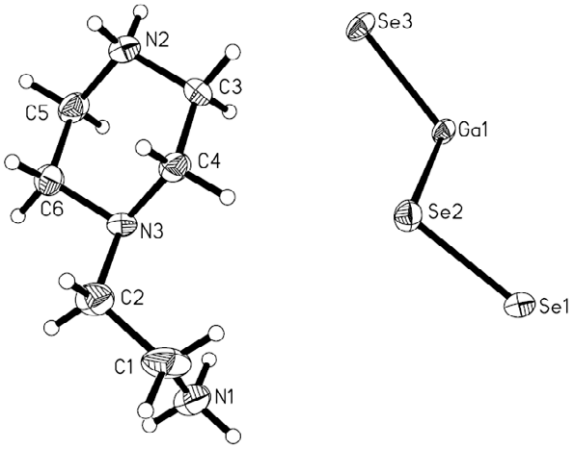

Figure S10. *ORTEP* plot showing the crystallographically asymmetric unit in **5**; thermal ellipsoids are given at the 30% probability level.

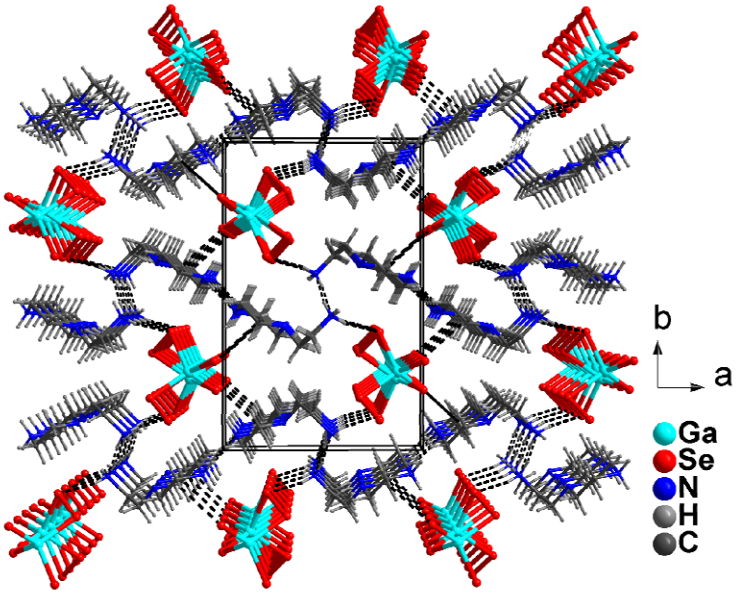

Figure S11. Perspective view of the structure of compound **5** along the *c*-axis; N–H···Se, C–H···Se and N–H···N hydrogen bonds are drawn in black dotted lines.

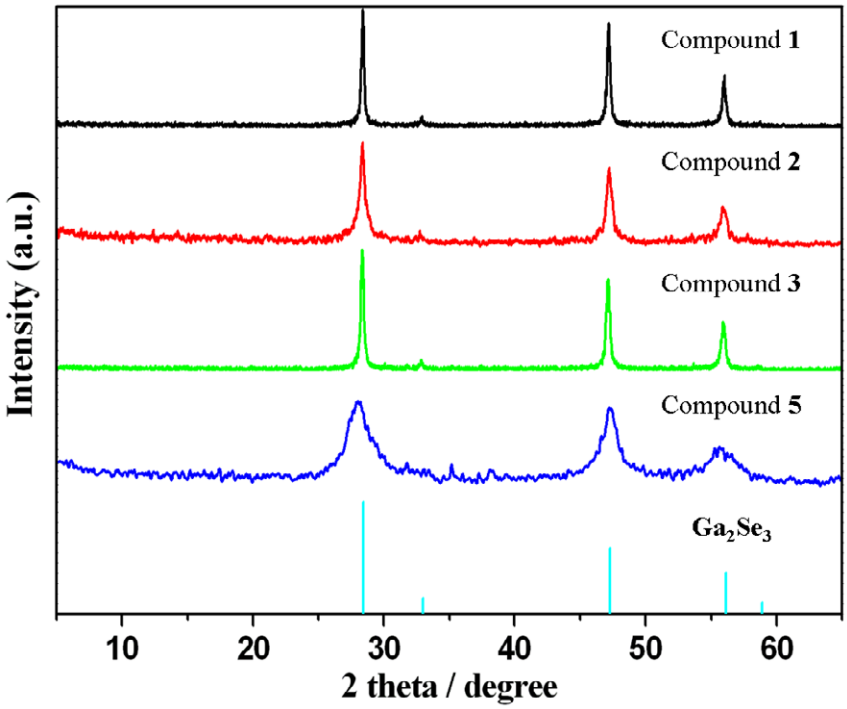

Figure S12. The PXRD patterns of the TGA residues of compounds **1** (black), **2** (red), **3** (green) and **5** (blue) are comparable to that of Ga_2Se_3 (blue-green).