Solvothermal synthesis, crystal structures and properties of three new thiogermanates: The only example of the thiogermanate anion $[Ge_2S_6]^{4-}$ as a bridging ligand to a lanthanide complex ion

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Table S1. Selected Bond Lengths (Å) and Angles (deg) for **1- 3**.

		1	
Ge1-S3	2.1477(13)	Ge1-S2#1	2.2678(10)
Ge1-S1	2.1638(11)	Ge1-S2	2.2796(11)
S3-Ge1-S1	115.69(4)	S3-Ge1-S2	111.30(4)
S3-Ge1-S2#1	112.54(5)	S1-Ge1-S2	110.33(5)
S1-Ge1-S2#1	110.38(4)	S2#1-Ge1-S2	94.67(4)
		2	
Eu1-N8	2.601(3)	Eu1-N5	2.623(3)
Eu1-N4	2.601(3)	Eu1-N6	2.623(3)
Eu1-N1	2.612(3)	Eu1-N3	2.623(3)
Eu1-N9	2.618(3)	Eu1-N2	2.633(3)
Eu1-N7	2.669(3)	Ge1-S3	2.2740(11)
Ge1-S1	2.1595(11)	Ge1-S3#2	2.2884(11)
Ge1-S2	2.1604(11)	N4-Eu1-N9	147.34(11)
N8-Eu1-N4	136.00(10)	N1-Eu1-N9	76.72(11)
N8-Eu1-N1	136.60(10)	N8-Eu1-N5	116.20(10)
N4-Eu1-N1	87.40(11)	N4-Eu1-N5	65.71(11)
N8-Eu1-N9	65.12(11)	N1-Eu1-N5	77.06(10)
N9-Eu1-N5	135.00(10)	N4-Eu1-N3	77.22(11)
N8-Eu1-N6	73.47(9)	N1-Eu1-N3	127.19(10)
N4-Eu1-N6	130.32(10)	N9-Eu1-N3	89.82(10)
N1-Eu1-N6	76.84(10)	N5-Eu1-N3	135.02(10)
N9-Eu1-N6	73.88(10)	N6-Eu1-N3	147.62(10)
N5-Eu1-N6	64.92(10)	N8-Eu1-N2	119.36(11)
N8-Eu1-N3	74.31(10)	N4-Eu1-N2	75.08(12)
N4-Eu1-N7	75.10(11)	N1-Eu1-N2	62.98(11)
N1-Eu1-N7	149.80(10)	N9-Eu1-N2	72.28(12)
N9-Eu1-N7	129.94(11)	N5-Eu1-N2	124.44(11)
N5-Eu1-N7	73.36(10)	N6-Eu1-N2	131.98(11)
N6-Eu1-N7	95.77(10)	N3-Eu1-N2	64.27(11)
N3-Eu1-N7	73.21(10)	N8-Eu1-N7	64.99(11)
N2-Eu1-N7	132.15(10)	S1-Ge1-S2	111.66(5)
S1-Ge1-S3#2	113.30(5)	S1-Ge1-S3	115.14(5)
S2-Ge1-S3#2	111.75(5)	S2-Ge1-S3	111.12(5)
S3-Ge1-S3#2	92.57(4)		
		3	
Y1-O1	2.248(8)	Y1-S3	2.870(3)

Y1-O1#3	2.297(6)	Y1-Y1#3	3.706(2)
Y1-N5	2.544(10)	Ge1-S1	2.173(3)
Y1-N3	2.564(9)	Ge1-S3	2.191(3)
Y1-N1	2.553(9)	Ge1-S2	2.273(4)
Y1-N4	2.573(12)	Ge1-S2#4	2.286(3)
Y1-N2	2.593(9)		
S1-Ge1-S3	115.45(12)	O1-Y1-O1#3	70.7(3)
S1-Ge1-S2	111.63(15)	O1-Y1-N5	150.3(3)
S3-Ge1-S2	110.94(13)	O1#3-Y1-N5	135.1(3)
S1-Ge1-S2#4	114.45(12)	O1-Y1-N3	84.4(3)
S3-Ge1-S2#4	108.76(14)	O1#3-Y1-N3	79.0(3)
S2-Ge1-S2#4	93.54(12)	N5-Y1-N3	111.7(4)
N3-Y1-N1	128.7(3)	O1-Y1-N1	74.9(3)
O1-Y1-N4	142.8(3)	O1#3-Y1-N1	132.8(3)
O1#3-Y1-N4	79.1(3)	N5-Y1-N1	75.6(4)
N5-Y1-N4	66.5(4)	N5-Y1-N2	75.3(4)
N3-Y1-N4	68.6(4)	N3-Y1-N2	66.0(3)
N1-Y1-N4	142.1(4)	N1-Y1-N2	67.5(3)
O1-Y1-N2	90.1(3)	N4-Y1-N2	101.1(4)
O1#3-Y1-N2	141.7(3)	O1-Y1-S3	100.64(17)
N4-Y1-S3	94.8(3)	O1#3-Y1-S3	79.96(17)
N2-Y1-S3	137.3(2)	N5-Y1-S3	75.3(2)
N1-Y1-S3	75.6(2)	N3-Y1-S3	155.4(2)

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

Table S2. Hydrogen bonds for **1** [Å and deg].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N4-H4C...S1#1	0.89(5)	2.49(5)	3.361(4)	169(4)
N4-H4B...S1#2	0.87(5)	2.48(5)	3.311(4)	160(4)
N2-H2G...S3#3	0.889(19)	2.71(3)	3.467(4)	143(4)
N2-H2G...S1#3	0.889(19)	2.85(4)	3.502(3)	131(4)
N4-H4A...S3#4	0.90(5)	2.46(5)	3.352(4)	179(4)
N2-H2F...S1#2	0.90(2)	2.56(2)	3.434(4)	165(4)
N2-H2E...N1#5	0.911(19)	2.06(3)	2.902(5)	153(5)

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

Table S3. Hydrogen bonds for **2** [Å and deg].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N1-H1A...S3#2	0.90	2.94	3.696(4)	143
N1-H1B...Cl1#2	0.90	2.69	3.422(4)	140
N2-H2C...S1#3	0.91	2.66	3.530(4)	160
N3-H3A...S2#1	0.90	2.57	3.472(4)	175
N4-H4A...S2#1	0.90	2.50	3.402(4)	175
N4-H4B...Cl1#4	0.90	2.60	3.398(4)	148
N5-H5C...S1#5	0.91	2.66	3.453(3)	146
N6-H6A...S2#2	0.90	2.51	3.358(3)	158
N6-H6B...Cl1#5	0.90	2.54	3.427(3)	170
N7-H7A...S2#1	0.90	2.95	3.783(4)	155
N8-H8C...Cl1#5	0.91	2.42	3.285(3)	160
N9-H9A...S2#2	0.90	2.53	3.386(4)	160
N9-H9B...S1#3	0.90	2.61	3.476(3)	163

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

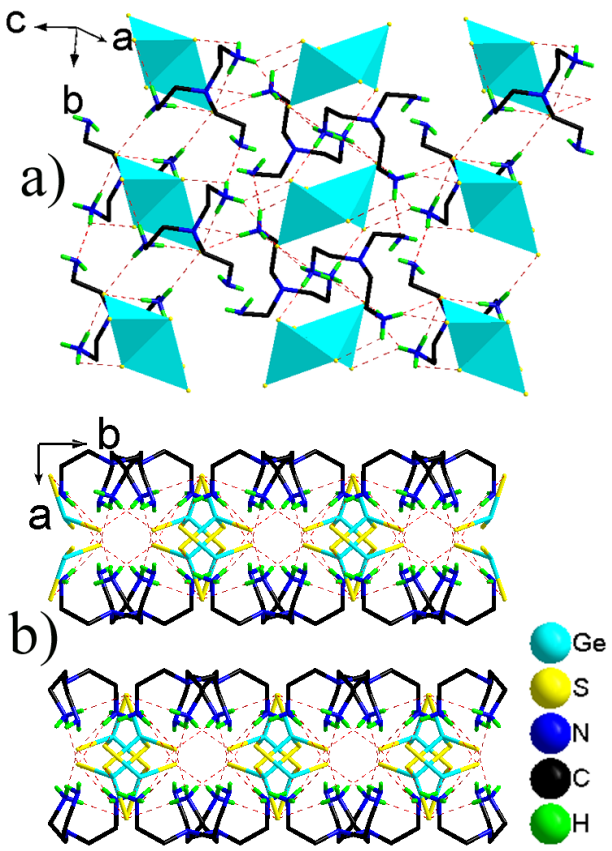

Figure S1 (a) Part of the crystal structure of **1**, showing the formation of a layer constructed from N-H…S hydrogen bonds. (b) View of the stacking mode for the layers in **1**. H atoms bonded to C atoms have been omitted for clarity.

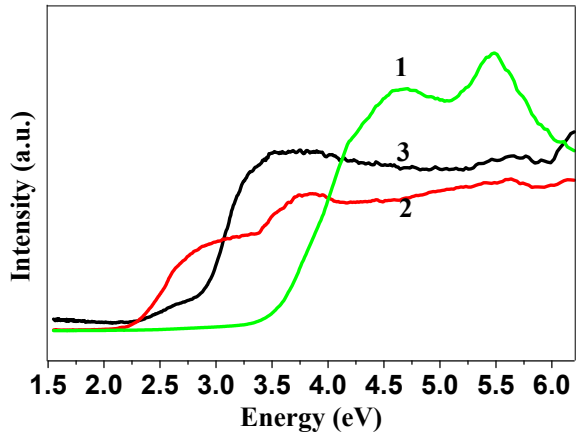

Figure S2 Solid-state optical absorption spectra of **1-3**.

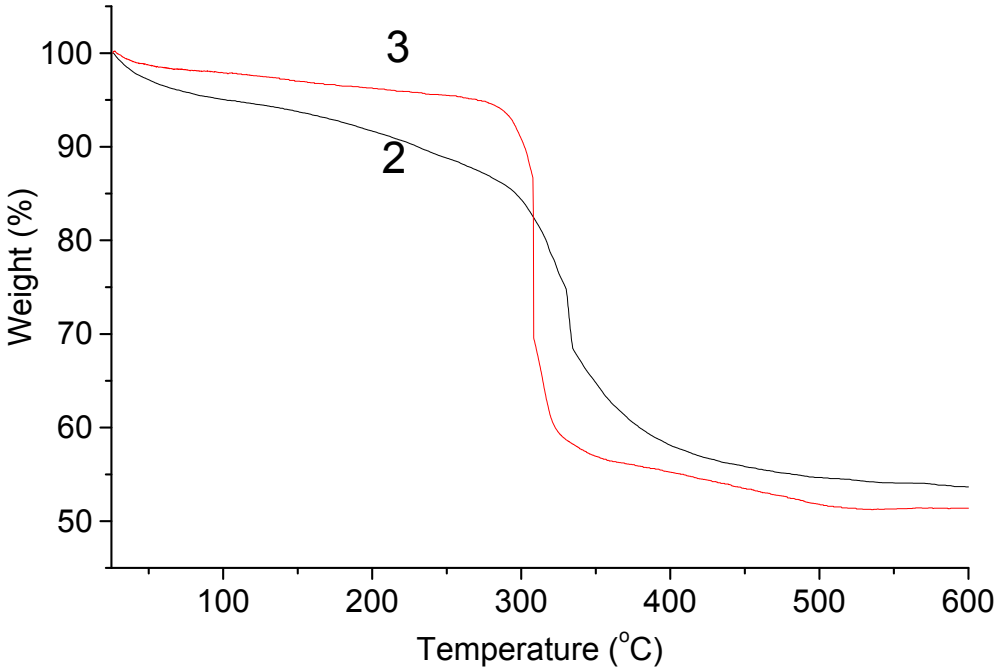

Figure S3 TG curves of **2** and **3**.