Supporting Information

$KNa_{0.78}Eu_{0.27}In_{3.80}B_{12}S_{12}$: A Novel Hexanary Thioborate Featuring $B_{12}S_{12}$ Cluster and Diverse InS_x (x = 4, 5, 6) Units

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Table S1. EDS analysis for **1**

Single crystal	#1	#2	#3
In	20.92	20.83	21.66
Eu	1.74	1.56	1.69
In/Eu	12.02	13.35	13.82

Table S2. The Rietveld powder XRD pattern refinement result.

	R(obs)	*wR*(obs)	*R*(all)	*wR*(all)	*R*p	*wR*p
value	4.35	5.25	4.36	5.26	3.19	4.27

Table S3. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (U_{eq}[a], Å^2 × 10^3) for **1**.

Atom	Wyck. site	*x*	*y*	*z*	U_{eq}/Å^2	SOF
K(1)	4*i*	3869.2(18)	0	8308.4(18)	47.1(6)	1
Na(1A)	4*i*	5487(5)	5000	4678(5)	42(2)	0.564
Na(1B)	2*c*	5000	5000	5000	42(2)	0.436
Eu(1)	4*f*	2500	2500	5000	35.6(7)	0.268
In(1)	4*e*	7500	2500	10000	20.7(3)	0.798
In(2)	4*i*	7563.8(4)	0	7464.1(4)	20.15(17)	1
In(3)	8*j*	5353.4(3)	2688.6(4)	7381.2(3)	23.33(15)	1
B(1)	4*i*	4953(6)	5000	8835(6)	16.4(19)	1
B(2)	4*i*	6151(6)	0	5349(6)	13.8(18)	1
B(3)	4*i*	5467(6)	0	6158(6)	12.9(18)	1
B(4)	8*j*	4456(4)	863(6)	5675(4)	13.9(13)	1
B(5)	4*i*	6027(6)	5000	9712(6)	14.6(19)	1
B(6)	8*j*	5315(4)	3622(6)	9558(4)	14.5(13)	1
B(7)	8*j*	4486(4)	1407(6)	4527(4)	12.7(12)	1
B(8)	8*j*	5853(4)	4142(6)	10716(4)	15.8(13)	1
S(1)	5*i*	5938.5(13)	0	7449.7(13)	16.6(4)	1
S(2)	4*i*	7430.2(13)	0	5754.8(13)	17.8(4)	1
S(3)	8*j*	3902.2(9)	1744.9(15)	6482.4(10)	19.1(3)	1
S(4)	4*i*	4820.5(15)	5000	7541.4(13)	21.6(5)	1
S(5)	8*j*	8233.1(9)	1837.5(14)	8501.7(10)	18.2(3)	1
S(6)	8*j*	6095.5(10)	2866.1(15)	6079.8(10)	21.2(3)	1
S(7)	8*j*	5689.3(10)	2126.2(14)	9094.0(10)	20.0(3)	1
S(8)	4*i*	7143.8(15)	5000	9412.6(16)	36.3(6)	1

[a] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table S4. Selected bond distances (Å) for **1**.[a]

Bond	Dist.	Bond	Dist.
Eu(1)–S(2)#8	2.8478(8)	B(1)–B(5)	1.799(12)
Eu(1)–S(2)#9	2.8478(8)	B(1)–B(6)#7	1.786(8)
Eu(1)–S(3)	2.7360(14)	B(1)–B(6)	1.786(8)
Eu(1)–S(3)#10	2.7360(14)	B(1)–B(8)#12	1.779(9)
Eu(1)–S(6)#5	2.9966(14)	B(1)–B(8)#13	1.779(9)
Eu(1)–S(6)#3	2.9966(14)	B(2)–B(3)	1.769(12)
K(1)–S(1)	3.687(3)	B(2)–B(4)#5	1.786(9)
K(1)–S(3)#1	3.243(2)	B(2)–B(4)#9	1.786(9)
K(1)–S(3)	3.243(2)	B(2)–B(7)#9	1.797(8)
K(1)–S(5)#2	3.4754(17)	B(2)–B(7)#5	1.797(8)
K(1)–S(5)#3	3.4754(17)	B(3)–B(4)#1	1.768(9)
K(1)–S(7)	3.508(2)	B(3)–B(4)	1.768(9)
K(1)–S(7)#1	3.508(2)	B(3)–B(7)#9	1.789(8)
K(1)–S(8)#2	3.425(3)	B(3)–B(7)#5	1.789(8)
Na(1A)–S(4)#4	3.155(7)	B(4)–B(4)#1	1.803(13)
Na(1A)–S(6)#5	3.261(6)	B(4)–B(7)#5	1.806(8)
Na(1A)–S(6)#7	3.007(5)	B(4)–B(7)	1.783(8)
Na(1A)–S(6)	3.007(5)	B(5)–B(6)	1.782(8)
Na(1A)–S(6)#4	3.261(6)	B(5)–B(6)#7	1.782(8)
In(1)–S(5)	2.7917(14)	B(5)–B(8)#7	1.796(9)
In(1)–S(5)#11	2.7917(14)	B(5)–B(8)	1.796(9)
In(1)–S(7)	2.7634(15)	B(6)–B(6)#12	1.798(12)
In(1)–S(7)#11	2.7634(15)	B(6)–B(8)	1.764(8)
In(1)–S(8)#11	2.7588(8)	B(6)–B(8)#12	1.805(8)
In(1)–S(8)	2.7588(8)	B(7)–B(7)#5	1.802(12)

In(2)–S(1)	2.474(2)	B(8)–B(8)#7	1.793(14)
In(2)–S(2)	2.4528(19)	B(1)–S(4)	1.849(9)
In(2)–S(5)#1	2.4946(15)	B(1)–S(4)#7	1.849(9)
In(2)–S(5)	2.4947(15)	B(2)–S(2)	1.886(9)
In(3)–S(1)	2.9409(8)	B(3)–S(1)	1.838(9)
In(3)–S(3)	2.4675(15)	B(4)–S(3)	1.863(6)
In(3)–S(4)#7	2.5778(9)	B(5)–S(8)	1.866(9)
In(3)–S(4)	2.5778(9)	B(6)–S(7)	1.852(6)
In(3)–S(6)	2.4596(14)	B(7)–S(6)#5	1.868(6)
In(3)–S(7)	2.4915(14)	B(8)–S(5)#11	1.863(6)

Symmetry codes: #1 +*x*, -*y*, +*z*; #2 -1/2+*x*, -1/2+*y*, +*z*; #3 -1/2+*x*, 1/2-*y*, +*z*; #4 1-*x*, 1-*y*, 1-*z*; #5 1-*x*, +*y*, 1-*z*; #6 1/2+*x*, 1/2+*y*, +*z*; #7 +*x*, 1-*y*, +*z*; #8 -1/2+*x*, 1/2+*y*, +*z*; #9 1-*x*, -*y*, 1-*z*; #10 1/2-*x*, 1/2-*y*, 1-*z*; #11 3/2-*x*, 1/2-*y*, 2-*z*; #12 1-*x*, +*y*, 2-*z*; #13 1-*x*, 1-*y*, 2-*z*.

Table S5. The incomplete occupations of Eu and In in literature.

Compounds	Occupancy	Ref.
$Eu_{1.836}Ta_{15}O_{32}$	0.306 for Eu	1
$Eu_{0.45}NbO_{3.175}$	0.45 for Eu	2
$Na_5CaIn_{1.67}Sb_4$	0.83 for In	3
$La_3In_{0.34}GeS_7$	0.341 for In	4

Table S6. The In–S distances in literature.

Compounds	*d*(In–S)/ Å	Ref.
$NaIn_3S_5$	2.504–2.929	5
$Ba_{18}F_{18}In_8S_{21}$	2.383–2.941	6
$Fe_{1.5}Pb_{5.5}In_{10}S_{22}$	2.479–2.952	7
$Ca_{0.76}In_{2.84}S_5$	2.479–2.916	8
$La_4Ag_2In_4S_{13}$	2.401–2.932	9

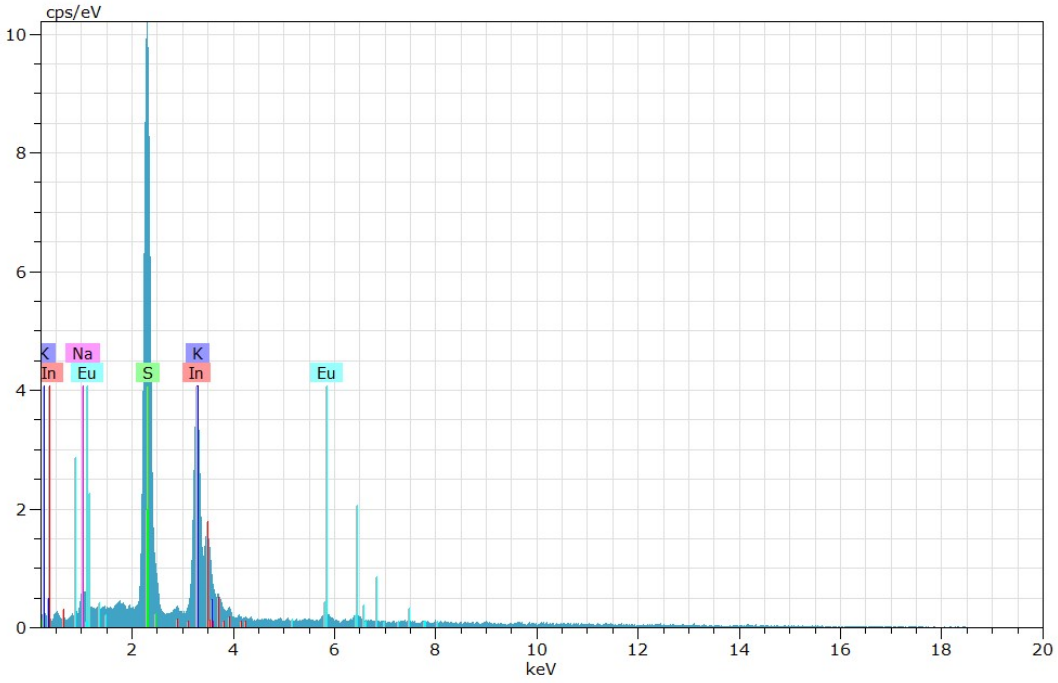

Fig. S1 EDS analysis for **1**.

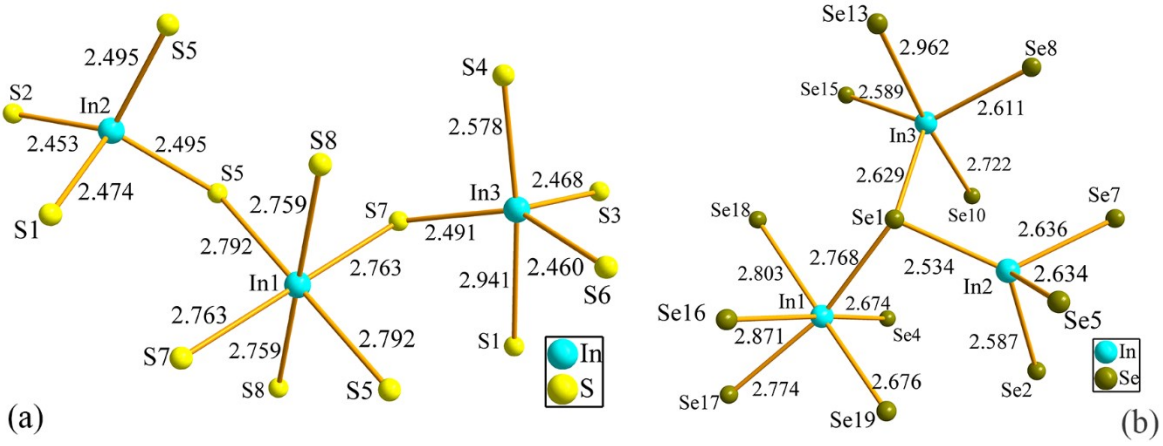

Fig. S2 Diverse InQ_x coordination styles in **1** (a) and $K_5In_3P_6Se_{19}$ (b).

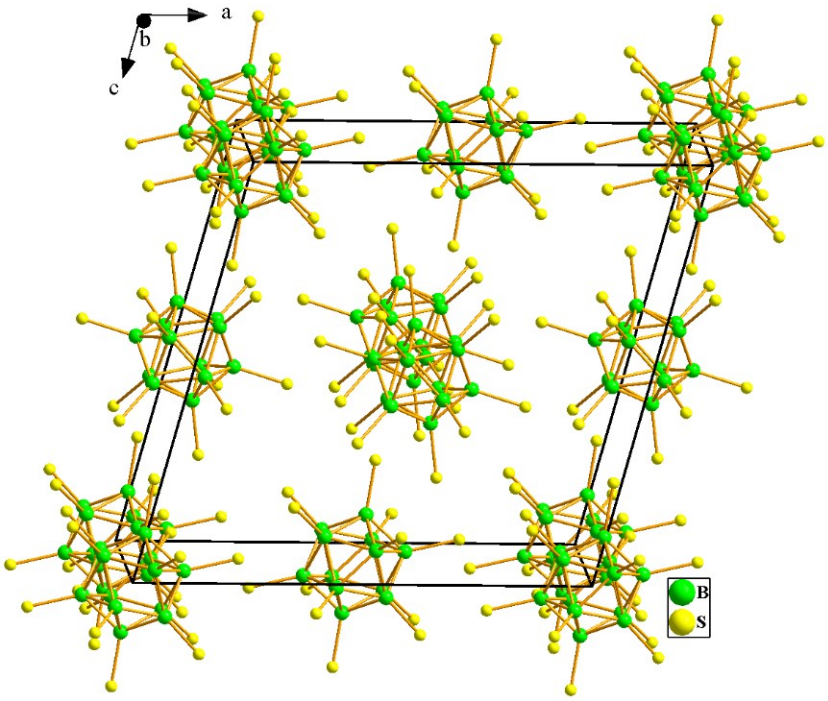

Fig. S3 The unit cell of $KNa_{0.78}Eu_{0.27}In_{3.80}B_{12}S_{12}$. For clarity, only those B and S atoms in the above.

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