Supporting Information

$[NH_3CH_3]_4[In_4SbS_9SH]$: A novel methylamine-directed indium thioantimonate with Rb^+ ion-exchange property

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Table S1. Summary of data collections and structure refinements for crystals **1Rb-1h**, **1Rb-2h**, and **1Rb-4h**.

	1Rb–1h	**1Rb–2h**	**1Rb–4h**
Empirical formula	$C_{3.6}H_{22.8}In_4N_{3.6}O_{0.1}Rb_{0.4}S_{10}Sb$	$C_{3.2}H_{20.6}In_4N_{3.2}O_{0.2}Rb_{0.8}S_{10}Sb$	$C_{2.75}H_{18.12}In_4N_{2.75}O_{0.3125}Rb_{1.25}S_{10}Sb$
Formula weight	1054.07	1077.23	1103.29
Crystal system	cubic	cubic	cubic
Space group	$P2_13$	$P2_13$	$P2_13$
T/K	296	296	296
λ/Å	0.71073	0.71073	0.71073
a/Å	13.8981(4)	13.8535(8)	13.7914(13)
b/Å	13.8981(4)	13.8535(8)	13.7914(13)
c/Å	13.8981(4)	13.8535(8)	13.7914(13)
α/°	90	90	90
β/°	90	90	90
γ/°	90	90	90
V/Å^3	2684.52(13)	2658.8(3)	2623.2(4)
Z	4	4	4
D_c/Mg·m^{-3}	2.608	2.691	2.794
μ/mm^{-1}	5.875	6.659	7.577
F(000)	1969	2002	2038
Measured refls.	2659	2751	2652
Independent refls.	1472	1781	1680
R_{int}	0.0224	0.0276	0.0293
No. of parameters	94	95	89
GOF	1.027	1.020	1.039
Flack parameter	-0.15(11)	0.11(12)	0.14(11)
[a]R_1, wR_2 [$I > 2\sigma(I)$]	0.0422, 0.1057	0.0611, 0.1452	0.0629, 0.1397
R_1, wR_2 (all data)	0.0616, 0.1198	0.0949, 0.1639	0.1239, 0.1644

[a]$R_1 = \sum||Fo|-|Fc||/\sum|Fo|$, w$R_2 = \{\sum w[(Fo)^2 - (Fc)^2]^2/\sum w[(Fo)^2]^2\}^{1/2}$.

Table S2. Summary of data collections and structure refinements for crystals **1Rb-6h**, **1Rb-12h** **1Rb-48h** and **1Cs-36h**.

	1Rb–6h	**1Rb–12h**	**1Rb–48h**	**1Cs-36h**
Empirical formula	$C_2H_{14}In_4N_2O_{0.50}$ $Rb_2S_{10}Sb$	$C_{1.3}H_{10.15}In_4N_{1.3}O_{0.675}$ $Rb_{2.7}S_{10}Sb$	$C_{0.7}H_{6.85}In_4N_{0.7}O_{0.825}$ $Rb_{3.3}S_{10}Sb$	$C_{3.71}H_{23.25}In_4N_{3.71}$ $Cs_{0.29}S_{10}Sb$
Formula weight	1146.72	1187.26	1222.00	1060.15
Crystal system	cubic	cubic	cubic	cubic
Space group	$P2_13$	$P2_13$	$P2_13$	$P2_13$
T/K	296	296	296	296
λ/Å	0.71073	0.71073	0.71073	0.71073
a/Å	13.6686(13)	13.5292(3)	13.4957(2)	13.9056(1)
b/Å	13.6686(13)	13.5292(3)	13.4957(2)	13.9056(1)
c/Å	13.6686(13)	13.5292(3)	13.4957(2)	13.9056(1)
α/°	90	90	90	90
β/°	90	90	90	90
γ/°	90	90	90	90
V/Å^3	2553.7(4)	2476.38(10)	2458.02(8)	2688.87(3)
Z	4	4	4	4
D_c/Mg·m^{-3}	2.983	3.184	3.302	2.616
μ/mm^{-1}	9.202	10.854	12.114	5.533
F(000)	2100	2157	2207	1974
Measured refls.	2501	2472	2402	22567
Independent refls.	1390	1333	1322	1927
Peak and hole/e Å^{-3}	1.051/-1.003	1.603/-1.008	1.188/-0.669	1.166/-0.912
R_{int}	0.0359	0.0340	0.0241	0.0510
No. of parameters	92	62	62	79
GOF	1.044	1.020	1.006	1.048
Flack parameter	0.09(9)	0.05(5)	0.00(2)	0.04(9)
[a]R_1, wR_2 [$I > 2\sigma(I)$]	0.0645, 0.1436	0.0570, 0.1177	0.0319, 0.0854	0.0409, 0.1227
R_1, wR_2 (all data)	0.1122, 0.1667	0.0892, 0.1308	0.0361, 0.0887	0.0456, 0.1275

[a]$R_1 = \sum||Fo|-|Fc||/\sum|Fo|$, w$R_2 = \{\sum w[(Fo)^2 - (Fc)^2]^2/\sum w[(Fo)^2]^2\}^{1/2}$.

Table S3. Selected bond lengths (Å) and angles (°) for compounds **1** and **1Rb-24h**.

1		**1Rb-24h**	
In(1)-S(2)#1	2.4462(19)	In(1)-S(2)#1	2.428(3)
In(1)-S(2)	2.4462(19)	In(1)-S(2)	2.428(3)
In(1)-S(2)#2	2.4462(19)	In(1)-S(2)#2	2.428(3)
In(1)-S(1)	2.476(4)	In(1)-S(1)	2.427(7)
In(2)-S(4)	2.4435(19)	In(2)-S(4)	2.425(3)
In(2)-S(2)	2.4542(19)	In(2)-S(2)	2.443(3)
In(2)-S(4)#1	2.4673(18)	In(2)-S(4)#1	2.440(3)
In(2)-S(3)	2.4754(17)	In(2)-S(3)	2.471(3)

Sb(1)-S(3)	2.4345(18)	Sb(1)-S(3)	2.431(3)
Sb(1)-S(3)#3	2.4345(18)	Sb(1)-S(3)#4	2.431(3)
Sb(1)-S(3)#4	2.4345(18)	Sb(1)-S(3)#5	2.431(3)
S(4)-In(2)#2	2.4673(18)	S(4)-In(2)#2	2.440(3)
S(2)#1-In(1)-S(2)	112.07(4)	S(2)#1-In(1)-S(2)	112.01(7)
S(2)#1-In(1)-S(2)#2	112.07(4)	S(2)#1-In(1)-S(2)#2	112.01(7)
S(2)-In(1)-S(2)#2	112.07(4)	S(2)-In(1)-S(2)#2	112.01(7)
S(2)#1-In(1)-S(1)	106.73(5)	S(1)-In(1)-S(2)#1	106.80(7)
S(2)-In(1)-S(1)	106.73(5)	S(1)-In(1)-S(2)	106.80(7)
S(2)#2-In(1)-S(1)	106.73(5)	S(1)-In(1)-S(2)#2	106.80(7)
S(4)-In(2)-S(2)	116.34(7)	S(4)-In(2)-S(2)	114.20(10)
S(4)-In(2)-S(4)#1	112.60(9)	S(4)-In(2)-S(4)#1	111.95(14)
S(2)-In(2)-S(4)#1	108.63(7)	S(4)#1-In(2)-S(2)	111.88(11)
S(4)-In(2)-S(3)	105.21(7)	S(4)-In(2)-S(3)	107.23(10)
S(2)-In(2)-S(3)	106.47(7)	S(2)-In(2)-S(3)	104.13(10)
S(4)#1-In(2)-S(3)	106.97(6)	S(4)#1-In(2)-S(3)	106.75(9)
S(3)-Sb(1)-S(3)#3	95.49(6)	S(3)-Sb(1)-S(3)#4	95.82(9)
S(3)-Sb(1)-S(3)#4	95.49(6)	S(3)-Sb(1)-S(3)#5	95.82(9)
S(3)#3-Sb(1)-S(3)#4	95.49(6)	S(3)#4-Sb(1)-S(3)#5	95.82(9)
In(1)-S(2)-In(2)	103.50(7)	In(1)-S(2)-In(2)	103.58(11)
Sb(1)-S(3)-In(2)	99.18(6)	Sb(1)-S(3)-In(2)	95.49(9)
In(2)-S(4)-In(2)#2	102.59(7)	In(2)-S(4)-In(2)#2	102.34(10)

Symmetry transformations used to generate equivalent atoms for **1**: #1 *y*+1/2, -*z*+1/2, -*x*+1; #2 -*z*+1, *x*-1/2, -*y*+1/2; #3 *z*+1/2, -*x*+3/2, -*y*+1; #4 -*y*+3/2, -*z*+1, *x*-1/2; for **1Rb-24h**: #1 *z*, *x*, *y*; #2 *y*, *z*, *x*; #3 *z*+1/2, -*x*+3/2, -*y*+1; #4 -*z*+1, *x*+1/2, -*y*+3/2; #5 *y*-1/2, -*z*+3/2, -*x*+1.

Table S4. N%, C%, H% analyses and ICP-OES results of the pristine compound **1** and the ion-exchanged products.

Exchanged Cations	**N, C, H analyses Experiment (%) (Calc.)**	**ICP-OES results**	**Estimated formulae**	**Exchange yield (%)**
compound **1**	5.32, 4.88, 2.14 (5.43, 4.66, 2.44)		/	/
Rb^+ exchange for 1h	4.73, 4.27, 2.22 (4.78, 4.10, 2.18)	$Rb_{0.45}In_{4.00}$	$Rb_{0.4}(NH_3CH_3)_{3.6}In_4SbS_9SH\cdot 0.1H_2O$	10
Rb^+ exchange for 2h	4.03, 3.71, 2.01 (4.16, 3.57, 1.93)	$Rb_{0.77}In_{4.00}$	$Rb_{0.8}(NH_3CH_3)_{3.2}In_4SbS_9SH\cdot 0.2H_2O$	20
Rb^+ exchange for 4h	3.37, 3.12, 1.74 (3.49, 2.99, 1.66)	$Rb_{1.22}In_{4.00}$	$Rb_{1.25}(NH_3CH_3)_{2.75}In_4SbS_9SH\cdot 0.3125H_2O$	31.3

Rb^+ exchange for 6h	2.25, 2.21, 1.22 (2.44, 2.09, 1.23)	$Rb_{1.71}In_{4.00}$	$Rb_2(NH_3CH_3)_2In_4SbS_9SH\cdot 0.5H_2O$	50
Rb^+ exchange for 12h	1.36, 1.38, 0.88 (1.53, 1.32, 0.86)	$Rb_{2.42}In_{4.00}$	$Rb_{2.7}(NH_3CH_3)_{1.3}In_4SbS_9SH\cdot 0.675H_2O$	67.5
Rb^+ exchange for 24h	0.76, 0.87, 0.34 (0.80, 0.69, 0.57)	$Rb_{3.35}In_{4.00}$	$Rb_{3.3}(NH_3CH_3)_{0.7}In_4SbS_9SH\cdot 0.825H_2O$	82.5
Rb^+ exchange for 36h	0.75, 0.95, 0.57 (0.90, 0.77, 0.61)	$Rb_{3.22}In_{4.00}$	$Rb_{3.22}(NH_3CH_3)_{0.78}In_4SbS_9SH\cdot 0.825H_2O$	80.5
Rb^+ exchange for 48h	0.74, 0.90, 0.57 (0.94, 0.81, 0.63)	$Rb_{3.18}In_{4.00}$	$Rb_{3.18}(NH_3CH_3)_{0.82}In_4SbS_9SH\cdot 0.825H_2O$	79.5
Na^+ exchange for 24h	5.04, 4.55, 1.98 (5.17, 4.43, 2.40)	$Na_{0.20}In_{4.00}$	$Na_{0.18}(NH_3CH_3)_{3.82}In_4SbS_9SH\cdot 0.4H_2O$	4.5
Na^+ exchange for 36h	4.90, 4.56, 2.43 (5.11, 4.38, 2.46)	$Na_{0.33}In_{4.00}$	$Na_{0.19}(NH_3CH_3)_{3.81}In_4SbS_9SH\cdot 0.8H_2O$	4.8
Na^+ exchange for 48h	4.76, 4.37, 2.43 (5.10, 4.37, 2.45)	$Na_{0.32}In_{4.00}$	$Na_{0.2}(NH_3CH_3)_{3.8}In_4SbS_9SH\cdot 0.8H_2O$	5.0
K^+ exchange for 24h	3.72, 3.50, 1.55 (4.07, 3.49, 1.97)	$K_{1.34}In_{4.00}$	$K_{0.95}(NH_3CH_3)_{3.05}In_4SbS_9SH\cdot 0.6H_2O$	23.8
K^+ exchange for 36h	3.68,3.49, 2.03 (3.87, 3.32, 1.92)	$K_{1.31}In_{4.00}$	$K_{1.09}(NH_3CH_3)_{2.91}In_4SbS_9SH\cdot 0.8H_2O$	27.3
K^+ exchange for 48h	3.63, 3.38, 1.99 (3.92, 3.36, 1.92)	$K_{1.23}In_{4.00}$	$K_{1.06}(NH_3CH_3)_{2.94}In_4SbS_9SH\cdot 0.7H_2O$	26.5
Cs^+ exchange for 24h	4.54, 4.17, 1.94 (4.77, 4.09, 2.21)	weak emission	$Cs_{0.35}(NH_3CH_3)_{3.65}In_4SbS_9SH\cdot 0.3H_2O$	8.8
Cs^+ exchange for 36h	4.87, 4.59, 2.15 (4.89, 4.20, 2.23)	weak emission	$Cs_{0.29}(NH_3CH_3)_{3.71}In_4SbS_9SH\cdot 0.1H_2O$	7.3
Cs^+ exchange for 48h	4.75, 4.39, 2.10 (4.87, 4.17, 2.23)	weak emission	$Cs_{0.3}(NH_3CH_3)_{3.7}In_4SbS_9SH\cdot 0.2H_2O$	7.5
$Rb^+ + Na^+$ exchange for 24h	0.70, 0.72, 0.61 (0.79, 0.67, 0.56)	$Na_{0.18}Rb_{2.61}In_{4.00}$	$Rb_{3.11}Na_{0.21}(NH_3CH_3)_{0.68}In_4SbS_9SH\cdot 0.83H_2O$	Rb^+: 77.8 Na^+: 5.2
$Rb^+ + K^+$ exchange for 24h	0.73, 0.73, 0.55 (0.76, 0.65, 0.55)	$K_{0.41}Rb_{2.18}In_{4.00}$	$Rb_{2.82}K_{0.53}(NH_3CH_3)_{0.65}In_4SbS_9SH\cdot 0.84H_2O$	Rb^+: 70.5 K^+: 13.3
$Rb^+ + Cs^+$ exchange for 24h	4.83, 4.12, 2.07 (4.83, 4.14, 2.20)	$Rb_{0.11}In_{4.00}$	$Rb_{0.11}Cs_{0.23}(NH_3CH_3)_{3.66}In_4SbS_9SH\cdot 0.09H_2O$	Rb^+: 2.8 Cs^+: 5.8
$Rb^+ + Na^+ + K^+$ exchange for 24h	0.50, 0.47, 0.59 (0.53,0.46,0.46)	$Na_{0.01}K_{0.44}Rb_{2.68}In_{4.00}$	$Rb_{3.03}Na_{0.01}K_{0.50}(NH_3CH_3)_{0.46}In_4SbS_9SH\cdot 0.885H_2O$	Rb^+: 75.8 Na^+: 0.25 K^+: 12.5
$Rb^+ + Na^+ + K^+ + Cs^+$ exchange for 24h	4.60, 4.12, 2.14 (4.62, 3.96, 2.12)	$Na_{0.03}K_{0.48}Rb_{0.10}In_{4.00}$	$Rb_{0.06}Na_{0.02}K_{0.32}Cs_{0.13}(NH_3CH_3)_{3.47}In_4SbS_9SH\cdot 0.13H_2O$	Rb^+: 1.5 Na^+: 0.5 K^+: 8.0 Cs^+: 3.3

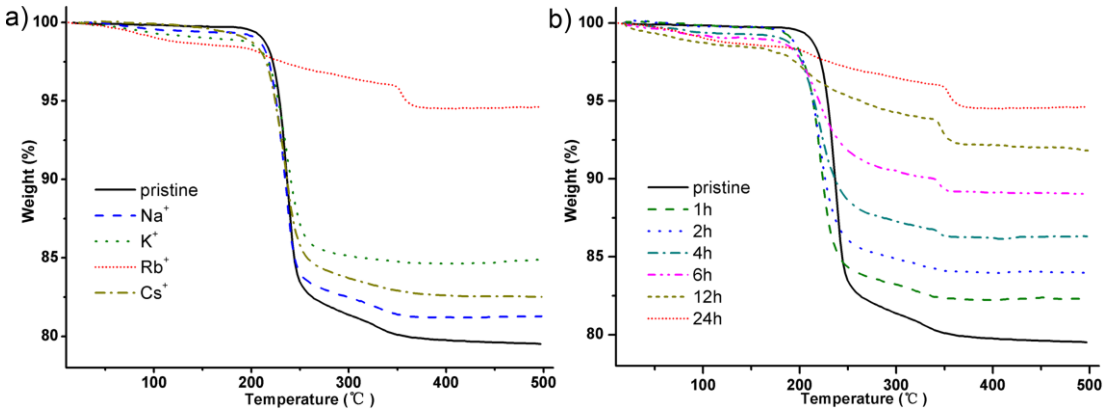

Figure S1. Thermogravimetric curves for (a) **1** and the 24h Na^+-, K^+-, Rb^+-, Cs^+-exchanged products and (b) **1** and the time-dependent Rb^+-exchanged products.

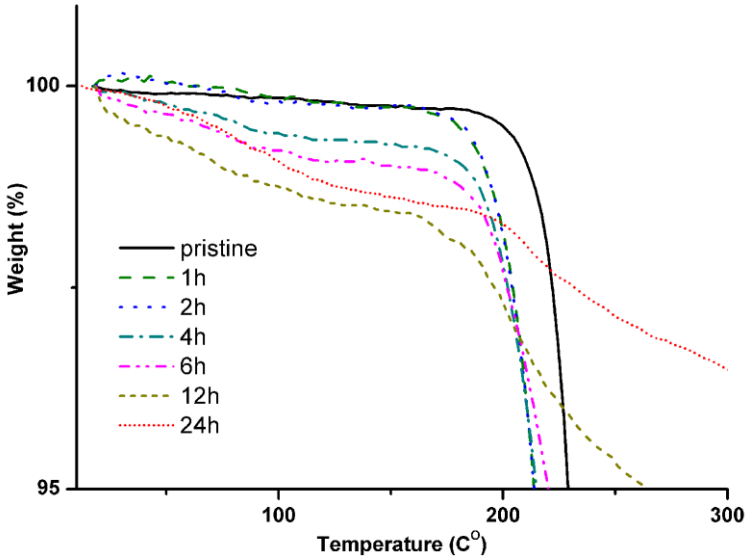

Figure S2. Thermogravimetric curves for **1** and the time-dependent Rb^+-exchanged products in the low-temperature region.

Table S5. Thermogravimetric analyses of **1** and the Na^+-, K^+-, Rb^+-, Cs^+-exchanged products in 24h.

Exchanged cation	**Estimated formula**	**Experimental weight loss at ~20–390°C (%)**	**Calculated weight loss (%)**
Pristine	\	20.16	20.31 (2.50 H_2S+4 CH_3NH_2)
Na^+	$Na_{0.18}(NH_3CH_3)_{3.82}In_4SbS_9SH{\cdot}0.4H_2O$	18.16	17.72 (1.91 H_2S+3.82 CH_3NH_2)
		0.62	0.61 (H_2O)
K^+	$K_{0.95}(NH_3CH_3)_{3.05}In_4SbS_9SH{\cdot}0.6H_2O$	14.35	13.98 (1.53 H_2S+3.05 CH_3NH_2)
		1.01	1.03 (H_2O)
Rb^+	$Rb_{3.3}(NH_3CH_3)_{0.7}In_4SbS_9SH{\cdot}0.825H_2O$	3.9	4.15 (0.85 H_2S+0.7 CH_3NH_2)
		1.54	1.22 (H_2O)

Cs^+	$Cs_{0.35}(NH_3CH_3)_{3.65}In_4SbS_9SH{\cdot}0.3H_2O$	16.91	16.37 (1.825 H_2S+3.65 CH_3NH_2)
		0.45	0.50 (H_2O)

Table S6. Thermogravimetric analyses of **1** and the time-dependent Rb^+-exchanged products.

Reaction time	**Estimated formula**	**Experimental weight losses at ~20–390°C (%)**	**Calculated weight losses (%)**
1h	$Rb_{0.4}(NH_3CH_3)_{3.6}In_4SbS_9SH{\cdot}0.1H_2O$	17.51	18.02 (2.3 H_2S+3.6 CH_3NH_2)
		0.24	0.17 (H_2O)
2h	$Rb_{0.8}(NH_3CH_3)_{3.2}In_4SbS_9SH{\cdot}0.2H_2O$	15.72	15.85 (2.1 H_2S+3.2 CH_3NH_2)
		0.24	0.33 (H_2O)
4h	$Rb_{1.25}(NH_3CH_3)_{2.75}In_4SbS_9SH{\cdot}0.3125H_2O$	12.99	13.52(1.875 H_2S+2.75 CH_3NH_2)
		0.75	0.51 (H_2O)
6h	$Rb_2(NH_3CH_3)_2In_4SbS_9SH{\cdot}0.5H_2O$	9.79	9.87 (1.5 H_2S+2 CH_3NH_2)
		1.04	0.78 (H_2O)
12h	$Rb_{2.7}(NH_3CH_3)_{1.3}In_4SbS_9SH{\cdot}0.675H_2O$	6.31	6.81 (1.15 H_2S+1.3 CH_3NH_2)
		1.48	1.02 (H_2O)
24h	$Rb_{3.3}(NH_3CH_3)_{0.7}In_4SbS_9SH{\cdot}0.825H_2O$	3.9	4.15 (0.85 H_2S+0.7 CH_3NH_2)
		1.54	1.22 (H_2O)