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Supporting Information

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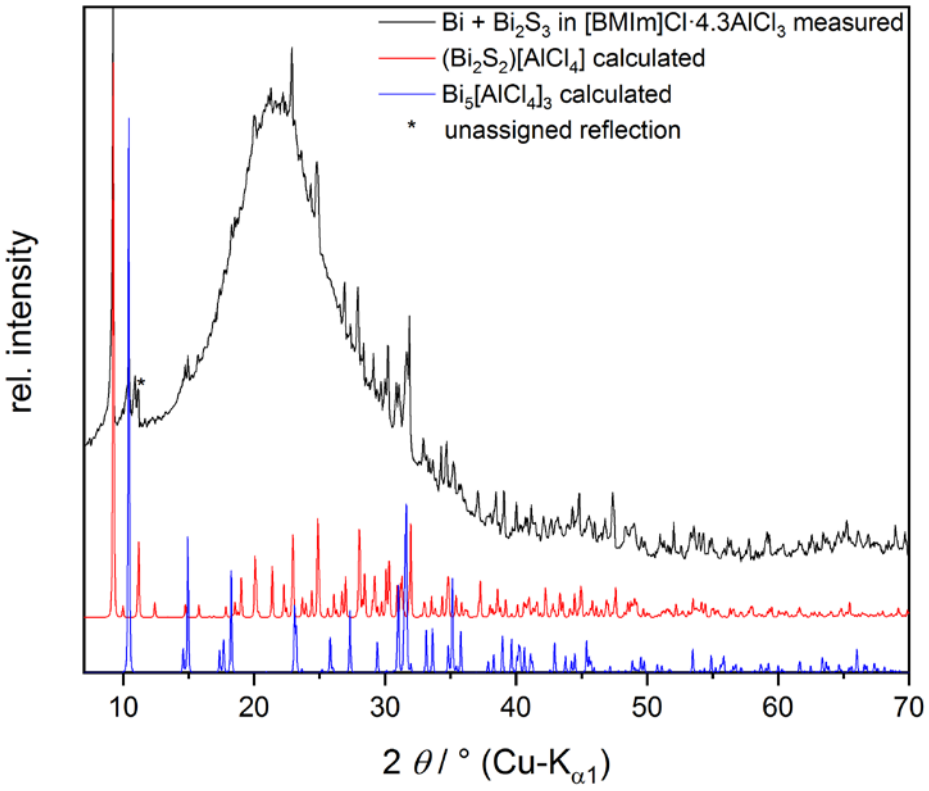

Figure S1. Powder diffractogram of the product of a synthesis yielding $(Bi_2S_2)[AlCl_4]$ (**1**) without further treatment. The high background, especially in the range $15° \leq 2\theta \leq 35°$, is caused by the glass capillaries used for the air-sensitive samples. The unassigned reflection is suspected to be caused by $(Bi_4S_4)[AlCl_4]_4$ but could not be confirmed beyond reasonable doubt due to the high background and overlap with the other diffraction patterns.

Table S1. Coordinates, coefficients U_{ij} (/ 10 pm^2) of the tensors of the anisotropic displacement, and equivalent displacement parameters for the atoms in $(Bi_2S_2)[AlCl_4]$. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor. All atoms occupy general Wyckoff positions 4*e*. The occupancy of positions denoted with A or B is ½.

Atom	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{eq}
Bi1	0.5233(1)	0.4334(1)	0.6068(1)	34(1)	36(1)	20(1)	3(1)	–5(1)	6(1)	30(1)
Bi2	0.2433(1)	0.3035(1)	0.4631(1)	35(1)	22(1)	25(1)	–3(1)	3(1)	2(1)	27(1)
Bi3	0.1646(1)	0.6179(1)	0.5668(1)	29(1)	49(1)	33(1)	–18(1)	1(1)	–5(1)	37(1)
Bi4	0.0275(1)	0.4231(1)	0.6494(1)	69(1)	45(1)	18(1)	3(1)	5(1)	10(1)	44(1)
S1	0.4758(2)	0.6293(2)	0.5479(2)	31(1)	30(1)	26(1)	–3(1)	–1(1)	6(1)	29(1)
S2	0.2867(2)	0.3629(2)	0.6144(2)	26(1)	48(2)	22(1)	–2(1)	1(1)	3(1)	32(1)
S3	0.2028(2)	0.5145(2)	0.4252(2)	24(1)	21(1)	22(1)	–1(1)	3(1)	0(1)	22(1)
S4	0.0153(2)	0.2860(2)	0.5232(2)	30(1)	24(1)	35(2)	–1(1)	4(1)	–2(1)	30(1)
Al1	0.2139(3)	0.3853(3)	0.1987(2)	53(2)	31(2)	22(2)	–10(2)	–3(2)	9(2)	36(1)
Cl1	0.2024(5)	0.5604(3)	0.1938(2)	144(4)	33(2)	46(2)	–5(2)	16(2)	24(2)	75(1)
Cl2	0.1900(3)	0.3050(2)	0.0808(2)	71(2)	42(2)	33(2)	–15(1)	2(2)	3(2)	49(1)
Cl3	0.0675(3)	0.3212(3)	0.2788(2)	55(2)	72(2)	46(2)	–19(2)	13(2)	3(2)	57(1)
Cl4	0.3856(3)	0.3406(3)	0.2571(2)	52(2)	49(2)	47(2)	–1(2)	–11(2)	–1(2)	50(1)
Al2	0.2699(4)	0.4877(3)	0.8633(2)	71(3)	31(2)	30(2)	6(2)	–6(2)	–2(2)	44(1)
Cl5	0.2749(4)	0.5974(3)	0.7575(2)	100(3)	45(2)	28(2)	10(1)	–9(2)	–14(2)	58(1)
Cl6A	0.449(2)	0.452(2)	0.906(2)	114(10)	124(13)	157(16)	71(11)	–74(11)	–7(9)	131(7)
Cl7A	0.167(2)	0.578(2)	0.9614(9)	151(12)	37(5)	47(7)	–14(4)	33(8)	–32(7)	78(4)
Cl8A	0.164(4)	0.349(2)	0.839(2)	160(20)	25(5)	56(10)	–2(5)	0(11)	–23(9)	80(8)
Cl6B	0.440(2)	0.201(2)	0.856(2)	77(8)	96(10)	155(15)	40(9)	7(9)	44(7)	109(5)
Cl7B	0.246(2)	0.563(2)	0.9764(8)	188(15)	40(5)	31(5)	–11(4)	14(8)	–38(9)	86(5)
Cl8B	0.132(4)	0.365(2)	0.839(2)	137(18)	84(17)	38(9)	10(11)	–33(10)	–76(14)	86(9)

Table S2. Refinement of Bi4 with split positions: significantly deviating interatomic distances *d* (/ pm) and bond strengths s_{Bi-S} in $(Bi_2S_2)[AlCl_4]$. Changes in other interatomic distances do not exceed the standard deviations of those given in Table S1.

atom pair		*d*	s_{Bi-S}	atom pair		*d*	s_{Bi-S}
Bi3	Bi4A	313(2)		Bi3	Bi4B	297(2)	
Bi4A	S2	304(2)	0.27	Bi4B	S2	274(2)	0.60
Bi4A	S3	274(2)	0.60	Bi4B	S3	302(2)	0.28
Bi4A	S4	258.6(8)	0.91	Bi4B	S4	263(2)	0.81

Table S3. Refinement of Bi4 with split positions: Coordinates, coefficients U_{ij} (/10 pm^2) of the tensors of the anisotropic displacement, and equivalent displacement parameters for Bi4. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor. All atoms occupy general Wyckoff positions 4*e*. Changes in other atomic parameters do not exceed the standard deviations of those given in Table S2.

Atom	*x*	*y*	*z*	*sof*	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{eq}
Bi4A	0.017(2)	0.4222(6)	0.6492(4)	0.62	46(2)	43(1)	18(1)	6(1)	3(1)	11(1)	36(1)
Bi4B	0.046(2)	0.424(1)	0.6500(7)	0.38	39(3)	49(1)	17(1)	–1(1)	6(2)	2(2)	35(1)