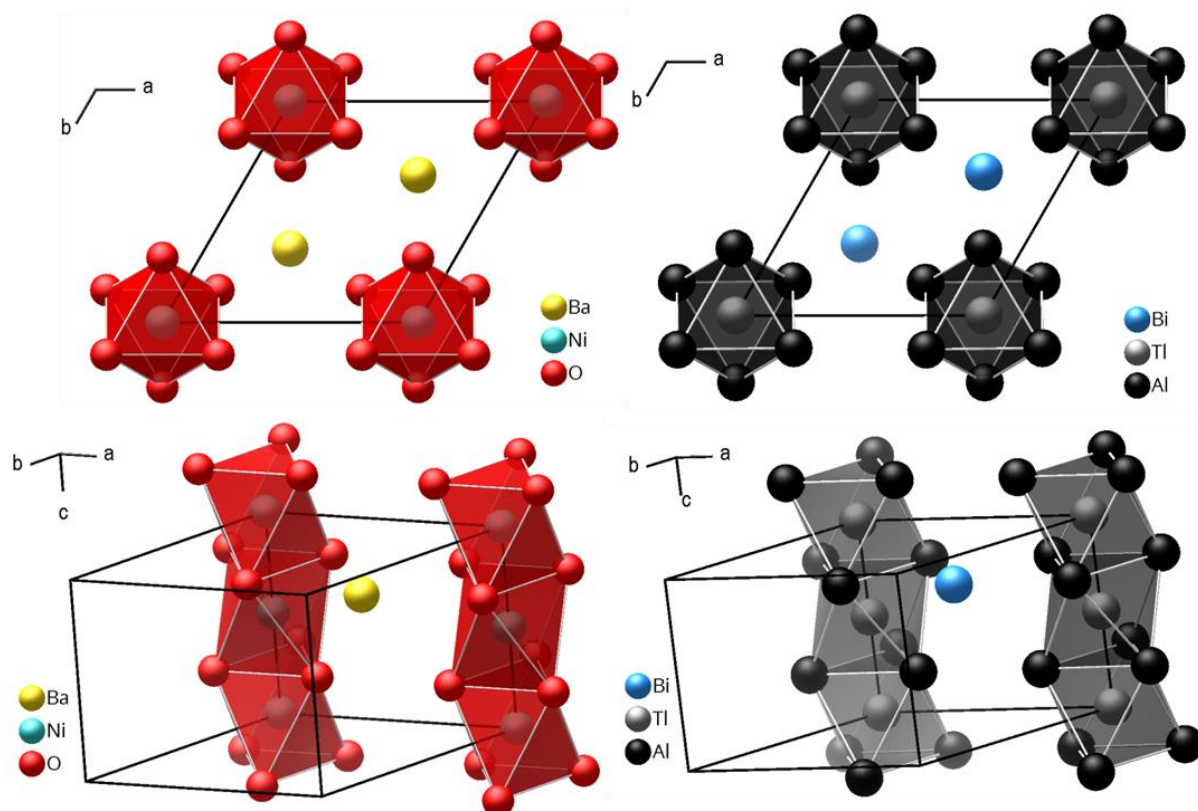# Supplementary Materials: Low-Temperature Ordering in the Cluster Compound (Bi₈)Tl[AlCl₄]₃

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Figure S1. Representation of structural motifs in $BaNiO_3$ (left) and $Bi_8Tl[AlCl_4]_3$ (right) according to the hexagonal perovskite structure type. For $Bi_8Tl[AlCl_4]_3$ Cl^- ions were omitted and all atomic radii were set to 1 Å for clarity. The bismuth atom represents the center of the Bi_8^{2+} polycation, while the Al^{3+} and Tl^+ positions remain unchanged.
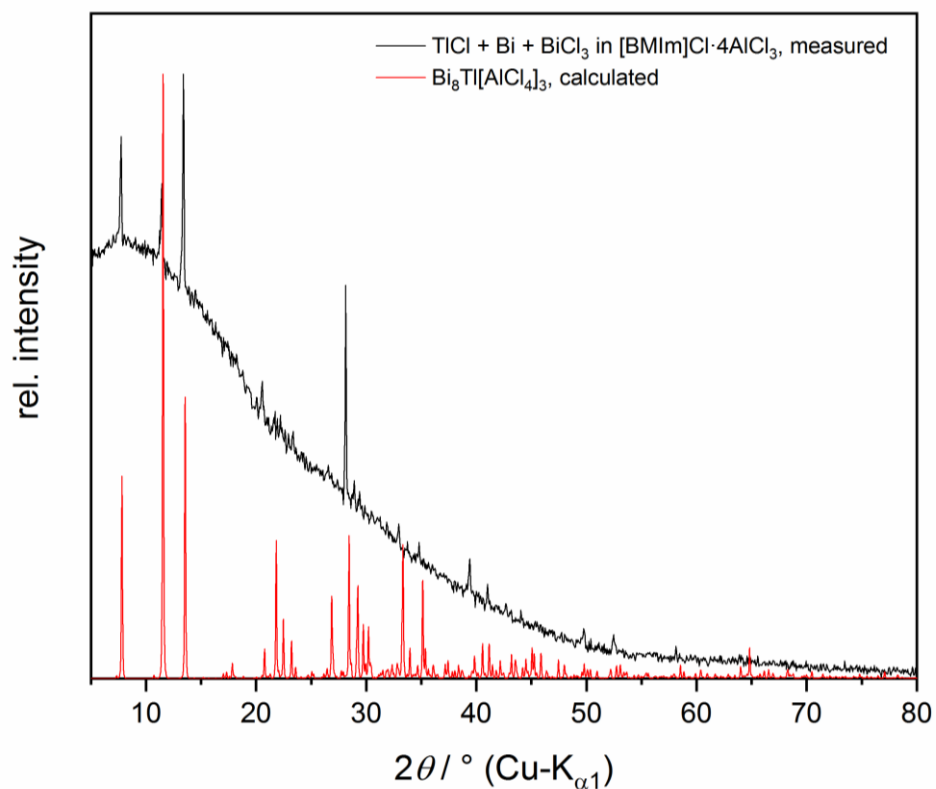
Figure S2. Powder diffractogram of a sample of $Bi_8Tl[AlCl_4]_3$ crystals that were separated mechanically and analysed without further treatment.
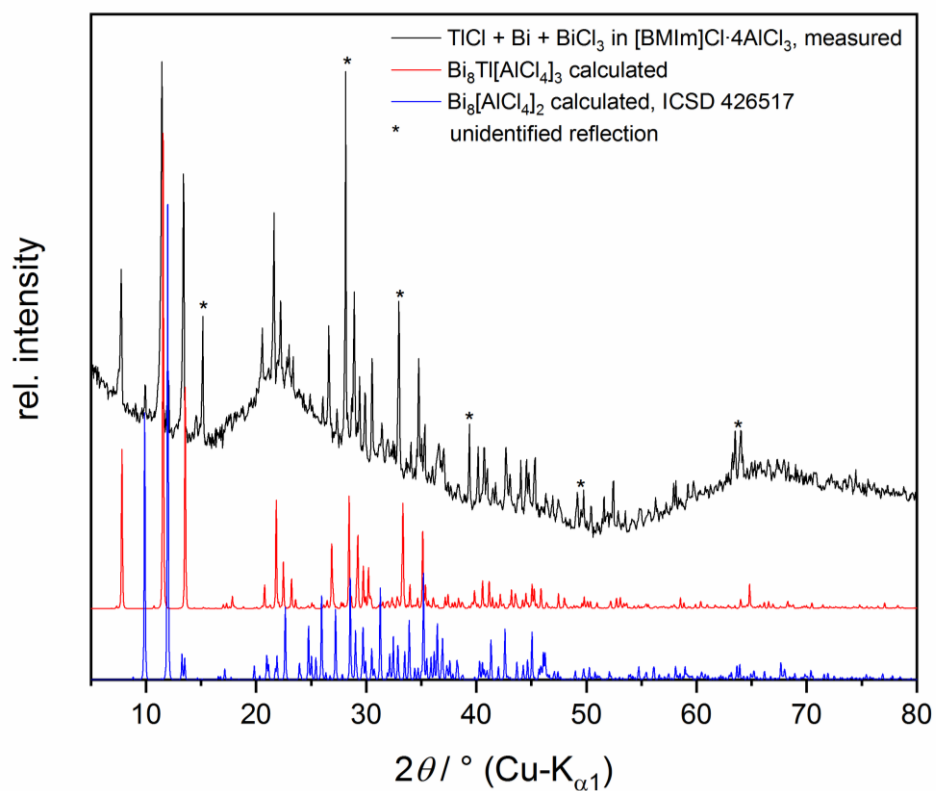
Figure S3. Powder diffractogram of the product of a $Bi_8Tl[AlCl_4]_3$ synthesis after treatment with dry DCM.

Table S1. Selected interatomic distances *d* (/ pm) in $(Bi_8)Tl[AlCl_4]_3$. Bismuth atom sites marked with * represent significant symmetry equivalent positions

atom pair		*d*		atom pair		*d*
Bi1	Bi2	302.5(2)		Bi3	Bi4	307.1(2)
Bi1	Bi2*	304.9(2)		Bi4	Bi4*	306.5(3)
Bi1	Bi3	307.6(3)		Tl1	Cl1	373.8(3)
Bi1	Bi4	305.0(3)		Tl1	Cl2	337.1(3)
Bi2	BI3	315.9(2)		Al1	Cl1	211.8(3)
Bi2	Bi4	309.8(2)		Al1	Cl2	211.8(5)
Bi3	Bi3*	305.0(3)		Al1	Cl3	211.7(6)

Table S2. Coordinates, coefficients U_{ij} (/ pm^2) of the tensors of the anisotropic displacement, and equivalent displacement parameters for the atoms in $(Bi_8)Tl[AlCl_4]_3$. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor. Special Wyckoff positions: Tl1 – 2*b*; Al1, Bi2, Cl2, Cl3 – 6*h*; general Wyckoff position 12*i* for Bi1, Bi3, Bi4, Cl1.

Atom	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{eq}
Bi1	0.7652(2)	0.3827(2)	0.4604(2)	108(1)	76(1)	72(1)	−29(1)	−66(1)	54(1)	82(1)
Bi2	0.7768(1)	0.5485(1)	0.25	78(1)	24(1)	99(1)	0	0	5(1)	76(1)
Bi3	0.5334(2)	0.1536(1)	0.3967(2)	88(1)	44(1)	48(1)	21(1)	17(1)	14(1)	68(1)
Bi4	0.5422(2)	0.3935(2)	0.3974(2)	86(1)	77(1)	56(1)	3(1)	31(1)	57(1)	66(1)
Tl1	0	0	0	73(1)	73(1)	24(1)	0	0	0	56(1)
Cl1	0.0648(2)	0.3060(2)	0.0818(2)	67(2)	68(2)	34(1)	3(1)	−10(1)	32(1)	57(1)
Cl2	0.1724(4)	0.1556(3)	0.25	84(3)	52(2)	41(2)	0	0	41(2)	56(1)
Cl3	0.3286(4)	0.4649(4)	0.25	60(3)	60(2)	49(2)	0	0	−3(2)	71(1)
Al1	0.1588(4)	0.3110(3)	0.25	44(2)	35(2)	34(2)	0	0	14(2)	37(1)

Additional discussion

In order to refine the structure in a space group matching the point group of the isolated Bi_8^{2+} clusters, we lowered the symmetry to the monoclinic space group *P* 1 1 2_1 (no. 4). The lattice parameters do not deviate significantly from the hexagonal refinement: *a* = 1303.3(1) pm, *b* = 1304.2(1) pm, *c* = 1039.9(1) pm and *γ* = 120°.

All previously equivalent interatomic distances were distinguished due to the absence of symmetry restrictions and the Al–Cl distances now show similar deviations to the ones reported for *M*[AlCl₄] (*M* = Li, Na, K) and $(Bi_8)[AlCl_4]_2$.[7,28–30] However, there are no major changes in the structure after the symmetry reduction. The three Bi_8^{2+} orientations were successfully isolated and their occupancy factors converged to ~33% each without any restrictions.

Table S3. Coordinates, coefficients U_{ij} (/ pm^2) of the tensors of the anisotropic displacement, and equivalent displacement parameters for the atoms in (Bi$_8$)Tl[AlCl$_4$]$_3$ at 170(2) K. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor. Only the main orientations of disordered bismuth positions are shown. Equal atomic displacement parameters were used for all aluminum atoms as well as equally oriented chloride ions.

Atom	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{eq}
Bi1	0.2755(2)	0.8906(2)	−0.0067(2)	23(2)	52(3)	78(3)	−11(3)	−7(3)	9(2)	55(1)
Bi2	0.1958(2)	0.8063(2)	0.0632(2)	75(4)	65(4)	62(3)	29(3)	−30(3)	24(3)	72(2)
Bi3	0.1086(2)	0.7286(2)	−0.0053(2)	68(4)	21(3)	74(5)	4(3)	−31(3)	22(3)	74(2)
Bi4	0.1877(2)	0.8116(2)	−0.0763(1)	51(3)	79(4)	40(3)	−31(2)	12(2)	13(3)	65(2)
Bi5	0.1934(2)	0.9265(2)	−0.0516(1)	95(4)	48(3)	68(3)	21(3)	−18(3)	28(3)	74(2)
Bi6	0.1991(2)	0.9249(2)	0.0464(1)	53(3)	42(3)	64(3)	−36(2)	7(2)	10(3)	59(2)
Bi7	0.0796(2)	0.8081(2)	0.0476(1)	35(3)	95(4)	53(3)	−3(3)	27(2)	3(3)	74(2)
Bi8	0.0747(2)	0.8102(2)	−0.0503(1)	53(3)	62(3)	49(3)	−16(2)	−26(2)	23(3)	57(2)
Bi9	0.6100(3)	0.8854(2)	−0.0035(2)	31(3)	53(4)	84(5)	4(4)	5(4)	35(3)	50(2)
Bi10	0.6915(3)	0.8855(3)	0.0670(2)	91(6)	93(6)	72(5)	−61(5)	−47(4)	59(6)	80(3)
Bi11	0.7719(3)	0.8795(3)	−0.0013(2)	30(5)	129(7)	104(7)	−7(7)	−16(5)	36(5)	89(3)
Bi12	0.6900(3)	0.8782(3)	−0.0730(2)	80(6)	112(6)	47(4)	49(4)	34(4)	63(5)	73(2)
Bi13	0.5741(2)	0.7690(3)	−0.0509(2)	50(5)	91(6)	65(4)	−33(4)	−29(4)	29(5)	72(2)
Bi14	0.5723(3)	0.7724(3)	0.0470(2)	60(5)	91(6)	68(4)	46(4)	43(4)	29(5)	77(2)
Bi15	0.6878(3)	0.7671(3)	0.0486(2)	116(7)	85(6)	45(4)	20(4)	−5(4)	82(5)	68(2)
Bi16	0.6893(3)	0.7647(3)	−0.0494(2)	87(6)	90(6)	36(3)	−15(4)	1(4)	63(5)	63(2)
Bi17	0.1148(2)	0.2250(2)	0.0026(2)	82(4)	25(3)	87(5)	4(3)	31(3)	34(3)	61(2)
Bi18	0.1198(2)	0.3096(2)	0.0724(2)	80(4)	58(3)	44(3)	4(2)	39(3)	32(3)	62(2)
Bi19	0.1196(2)	0.3923(2)	0.0034(2)	96(4)	86(4)	91(3)	−14(4)	−17(4)	79(3)	76(2)
Bi20	0.1158(2)	0.3083(2)	−0.0677(2)	124(5)	110(5)	58(3)	−43(3)	−58(3)	88(5)	85(2)
Bi21	0.2270(2)	0.3029(2)	−0.0506(1)	58(4)	65(4)	43(3)	−19(2)	6(2)	33(3)	54(2)
Bi22	0.2317(2)	0.3036(2)	0.0474(1)	88(4)	100(4)	61(3)	−19(3)	−39(3)	80(4)	68(2)
Bi23	0.2359(2)	0.4239(2)	0.0490(1)	38(3)	27(3)	49(2)	−18(2)	−11(2)	−9(2)	49(1)
Bi24	0.2307(3)	0.4222(2)	−0.0491(1)	130(6)	61(4)	32(3)	25(2)	28(3)	34(4)	80(2)
Bi25	0.6112(2)	0.3868(1)	0.0026(1)	115(4)	77(3)	67(3)	−10(3)	−1(3)	83(3)	71(2)
Bi26	0.6936(2)	0.3818(2)	0.0700(1)	67(3)	92(4)	62(3)	−57(3)	−31(2)	38(3)	74(2)
Bi27	0.7728(1)	0.3807(2)	−0.0013(1)	22(3)	91(4)	95(3)	7(3)	5(3)	10(3)	77(2)
Bi28	0.6900(2)	0.3848(2)	−0.0699(1)	73(3)	115(4)	65(3)	65(3)	34(2)	62(3)	78(2)
Bi29	0.5738(2)	0.2743(2)	−0.0507(1)	58(3)	85(3)	35(2)	−13(2)	−25(2)	31(3)	62(1)
Bi30	0.5743(2)	0.2700(2)	0.0474(1)	34(3)	74(3)	51(3)	29(2)	17(2)	7(2)	62(1)
Bi31	0.6898(2)	0.2650(2)	0.0454(1)	105(4)	69(3)	57(2)	20(2)	3(3)	69(3)	66(1)
Bi32	0.6888(2)	0.2694(2)	−0.0526(1)	119(4)	116(4)	34(2)	−19(3)	−6(2)	92(4)	75(2)
Tl1	0.0035(2)	−0.0046(2)	0.0817(1)	58(3)	45(3)	22(3)	0(2)	−2(2)	24(3)	42(1)
Tl2	0.4973(2)	0.0036(2)	0.0822(2)	57(3)	51(3)	22(1)	0(3)	1(3)	30(3)	42(1)
Tl3	0.4945(2)	0.4969(2)	0.0820(1)	56(3)	87(4)	24(3)	4(2)	1(2)	40(3)	54(2)
Tl4	0.0073(2)	0.5064(2)	0.0828(1)	69(4)	51(3)	22(2)	0(2)	2(2)	26(3)	50(2)
Cl1	0.420(2)	0.927(2)	−0.0016(7)	30(3)	46(3)	36(1)	−4(3)	0(3)	18(3)	38(1)
Cl2	0.329(2)	0.776(2)	0.0011(6)	43(4)	48(4)	46(1)	−4(3)	2(2)	34(3)	40(1)

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Cl3	0.468(2)	0.8446(9)	0.0530(6)	66(4)	50(4)	29(2)	4(3)	11(3)	28(4)	49(1)
Cl4	0.4625(9)	0.8444(9)	−0.0583(6)	43(4)	53(4)	19(2)	8(3)	−5(3)	26(4)	38(1)
Cl5	0.516(2)	0.1032(9)	−0.0012(7)	30(3)	46(3)	36(1)	−4(3)	0(3)	18(3)	38(1)
Cl6	0.426(2)	0.166(2)	0.0012(7)	43(4)	48(4)	46(1)	−4(3)	2(2)	34(3)	40(1)
Cl7	0.379(2)	0.034(2)	0.0517(6)	66(4)	50(4)	29(2)	4(3)	11(3)	28(4)	49(1)
Cl8	0.385(2)	0.038(2)	−0.0600(7)	43(4)	53(4)	19(2)	8(3)	−5(3)	26(4)	38(1)
Cl9	0.002(2)	0.580(2)	−0.0044(7)	30(3)	46(3)	36(1)	−4(3)	0(3)	18(3)	38(1)
Cl10	−0.0786(9)	0.657(2)	−0.0011(6)	43(4)	48(4)	46(1)	−4(3)	2(2)	34(3)	40(1)
Cl11	−0.1307(9)	0.5253(9)	0.0529(6)	66(4)	50(4)	29(2)	4(3)	11(3)	28(4)	49(1)
Cl12	−0.1275(9)	0.5214(8)	−0.0551(6)	43(4)	53(4)	19(2)	8(3)	−5(3)	26(4)	38(1)
Cl13	0.0810(9)	0.4984(9)	−0.0054(6)	30(3)	46(3)	36(1)	−4(3)	0(3)	18(3)	38(1)
Cl14	0.2381(9)	0.5814(9)	0.0005(6)	43(4)	48(4)	46(1)	−4(3)	2(2)	34(3)	40(1)
Cl15	0.153(2)	0.6321(8)	0.0492(6)	66(4)	50(4)	29(2)	4(3)	11(3)	28(4)	49(1)
Cl16	0.155(2)	0.625(2)	−0.0609(6)	43(4)	53(4)	19(2)	8(3)	−5(3)	26(4)	38(1)
Cl17	0.920(2)	0.928(2)	−0.0037(6)	30(3)	46(3)	36(1)	−4(3)	0(3)	18(3)	38(1)
Cl18	0.8289(6)	0.7776(6)	−0.0022(5)	43(4)	48(4)	46(1)	−4(3)	2(2)	34(3)	40(1)
Cl19	0.9766(9)	0.8521(9)	0.0477(5)	66(4)	50(4)	29(2)	4(3)	11(3)	28(4)	49(1)
Cl20	0.9672(8)	0.8550(7)	−0.0632(5)	43(4)	53(4)	19(2)	8(3)	−5(3)	26(4)	38(1)
Cl21	0.5152(7)	0.5971(6)	0.0005(6)	30(3)	46(3)	36(1)	−4(3)	0(3)	18(3)	38(1)
Cl22	0.427(2)	0.661(2)	−0.0043(7)	43(4)	48(4)	46(1)	−4(3)	2(2)	34(3)	40(1)
Cl23	0.382(2)	0.537(2)	0.0565(7)	66(4)	50(4)	29(2)	4(3)	11(3)	28(4)	49(1)
Cl24	0.3851(9)	0.5285(9)	−0.0555(6)	43(4)	53(4)	19(2)	8(3)	−5(3)	26(4)	38(1)
Cl25	0.571(2)	−0.008(2)	−0.0024(6)	30(3)	46(3)	36(1)	−4(3)	0(3)	18(3)	38(1)
Cl26	0.7320(9)	0.0732(9)	0.0002(6)	43(4)	48(4)	46(1)	−4(3)	2(2)	34(3)	40(1)
Cl27	0.655(2)	0.121(2)	0.0528(6)	66(4)	50(4)	29(2)	4(3)	11(3)	28(4)	49(1)
Cl28	0.6506(9)	0.1167(9)	−0.0586(6)	43(4)	53(4)	19(2)	8(3)	−5(3)	26(4)	38(1)
Cl29	0.087(2)	−0.013(2)	−0.0015(6)	30(3)	46(3)	36(1)	−4(3)	0(3)	18(3)	38(1)
Cl30	0.2341(8)	0.0642(7)	−0.0012(6)	43(4)	48(4)	46(1)	−4(3)	2(2)	34(3)	40(1)
Cl31	0.155(2)	0.118(2)	0.0565(8)	66(4)	50(4)	29(2)	4(3)	11(3)	28(4)	49(1)
Cl32	0.1488(9)	0.1165(9)	−0.0570(6)	43(4)	53(4)	19(2)	8(3)	−5(3)	26(4)	38(1)
Cl33	0.4083(7)	0.4181(9)	−0.0006(7)	30(3)	46(3)	36(1)	−4(3)	0(3)	18(3)	38(1)
Cl34	0.3382(8)	0.2581(8)	−0.0031(6)	43(4)	48(4)	46(1)	−4(3)	2(2)	34(3)	40(1)
Cl35	0.465(2)	0.3427(9)	0.0506(6)	66(4)	50(4)	29(2)	4(3)	11(3)	28(4)	49(1)
Cl36	0.463(2)	0.349(2)	−0.0596(6)	43(4)	53(4)	19(2)	8(3)	−5(3)	26(4)	38(1)
Cl37	0.008(2)	0.082(2)	−0.0004(7)	30(3)	46(3)	36(1)	−4(3)	0(3)	18(3)	38(1)
Cl38	−0.0581(8)	0.1686(9)	−0.0024(7)	43(4)	48(4)	46(1)	−4(3)	2(2)	34(3)	40(1)
Cl39	−0.1284(9)	0.0353(8)	0.0508(5)	66(4)	50(4)	29(2)	4(3)	11(3)	28(4)	49(1)
Cl40	−0.1159(8)	0.0361(8)	−0.0615(5)	43(4)	53(4)	19(2)	8(3)	−5(3)	26(4)	38(1)
Cl41	0.573(2)	0.489(2)	−0.0007(7)	30(3)	46(3)	36(1)	−4(3)	0(3)	18(3)	38(1)
Cl42	0.7220(9)	0.5489(8)	−0.0038(6)	43(4)	48(4)	46(1)	−4(3)	2(2)	34(3)	40(1)
Cl43	0.6650(8)	0.6257(8)	0.0508(5)	66(4)	50(4)	29(2)	4(3)	11(3)	28(4)	49(1)
Cl44	0.6509(8)	0.6146(8)	−0.0619(5)	43(4)	53(4)	19(2)	8(3)	−5(3)	26(4)	38(1)
Cl45	0.919(2)	0.421(2)	0.0032(7)	30(3)	46(3)	36(1)	−4(3)	0(3)	18(3)	38(1)
Cl46	0.843(2)	0.2668(9)	−0.0013(7)	43(4)	48(4)	46(1)	−4(3)	2(2)	34(3)	40(1)
Cl47	0.973(2)	0.3519(9)	−0.0572(6)	66(4)	50(4)	29(2)	4(3)	11(3)	28(4)	49(1)

Cl48	0.9735(8)	0.3385(8)	0.0571(5)	43(4)	53(4)	19(2)	8(3)	−5(3)	26(4)	38(1)
Al1	0.419(3)	0.845(3)	0.0006(8)	29(5)	33(5)	18(1)	−3(4)	−7(3)	12(5)	28(1)
Al2	0.426(3)	0.084(3)	−0.0012(8)	29(5)	33(5)	18(1)	−3(4)	−7(3)	12(5)	28(1)
Al3	−0.086(3)	0.572(3)	−0.0007(7)	29(5)	33(5)	18(1)	−3(4)	−7(3)	12(5)	28(1)
Al4	0.159(3)	0.582(3)	−0.0046(8)	29(5)	33(5)	18(1)	−3(4)	−7(3)	12(5)	28(1)
Al5	0.921(3)	0.849(3)	−0.0037(8)	29(5)	33(5)	18(1)	−3(4)	−7(3)	12(5)	28(1)
Al6	0.427(3)	0.580(3)	0.0015(8)	29(5)	33(5)	18(1)	−3(4)	−7(3)	12(5)	28(1)
Al7	0.653(3)	0.076(3)	−0.0014(7)	29(5)	33(5)	18(1)	−3(4)	−7(3)	12(5)	28(1)
Al8	0.158(3)	0.073(3)	−0.0003(7)	29(5)	33(5)	18(1)	−3(4)	−7(3)	12(5)	28(1)
Al9	0.417(3)	0.342(3)	−0.0019(8)	29(5)	33(5)	18(1)	−3(4)	−7(3)	12(5)	28(1)
Al10	−0.075(3)	0.079(3)	−0.0012(7)	29(5)	33(5)	18(1)	−3(4)	−7(3)	12(5)	28(1)
Al11	0.655(3)	0.569(3)	−0.0027(7)	29(5)	33(5)	18(1)	−3(4)	−7(3)	12(5)	28(1)
Al12	0.929(3)	0.344(3)	0.0013(7)	29(5)	33(5)	18(1)	−3(4)	−7(3)	12(5)	28(1)