Acta Cryst E CRYSTALLOGRAPHIC COMMUNICATIONS

ISSN 2056-9890

Growth and characterization of a new inorganic metal–halide crystal structure, $InPb_2Cl_5$

Michael P. Lewis, Ramjee Kandel, Gabriele Schatte and Peng L. Wang*

Department of Chemistry, Queen's University, Kingston, Ontario K7L 3N6, Canada. *Correspondence e-mail: wang.peng@chem.queensu.ca

Received 11 July 2023
Accepted 8 September 2023

Edited by S. Parkin, University of Kentucky, USA

Keywords: crystal structure; inorganic; $InPb_2Cl_5$; solid-state.

CCDC reference: 2294068

Supporting information: this article has supporting information at journals.iucr.org/e

A new solid-state inorganic compound, indium dilead pentachloride, $InPb_2Cl_5$, was synthesized by melting InCl and $PbCl_2$ in a vacuum-sealed quartz ampoule. The ampoule was heated to 793 K and then slowly cooled to room temperature to induce crystallization of $InPb_2Cl_5$. $InPb_2Cl_5$ crystallizes in the monoclinic crystal system adopting a space group of type $P2_1/c$, which is isostructural with other metal halides such as $RbPb_2Cl_5$, KPb_2Cl_5 and $TlPb_2Cl_5$. The bulk $InPb_2Cl_5$ exhibits a metallic black/grey colour, allowing it to be separated from white/yellow $PbCl_2$ crystals. Due to the incongruent nature of the compound, the pure bulk $InPb_2Cl_5$ was not obtained. The black/grey $InPb_2Cl_5$ crystals were characterized by powder and single-crystal X-ray diffraction. $InPbCl_3$ was also explored, however the growth was unsuccessful.

1. Chemical context

Indium lead chloride, $InPb_2Cl_5$ is a metal halide that has been studied as a new material to be used in optoelectronic semiconducting applications. Other isostructural metal halides that have the structure APb_2Cl_5 (where A = K, Rb, Tl) have gained interest in fields such as optoelectronics (Vu *et al.*, 2020), and photovoltaics as a tunable laser (Isaenko *et al.*, 2013; Khyzhun *et al.*, 2014; Brown *et al.*, 2013). There has been success in growing metal-halide semiconducting crystals such as $RbPb_2Cl_5$ and KPb_2Cl_5 (Isaenko *et al.*, 2013; Rowe *et al.*, 2014; Isaenko *et al.*, 2009), however single-crystal $InPb_2Cl_5$ has not been reported and has only been computationally studied as the $InPbCl_3$ phase (Khan *et al.*, 2022). Similar to $RbPb_2Cl_5$, KPb_2Cl_5, and $TlPb_2Cl_5$, $InPb_2Cl_5$ crystallizes in a monoclinic structure and has a space group of type $P2_1/c$. Bulk $InPb_2Cl_5$ samples were prepared, which contained a mixture of black/grey metallic polycrystalline $InPb_2Cl_5$ at the bottom of the ampoule and white/yellow $PbCl_2$ crystals above. When the black/grey crystals were broken up, the crystals appeared to have a much clearer and lighter green hue. The broken-up crystal was examined under an optical microscope and clear colourless crystal pieces were seen. The clear colourless single-crystal pieces were handpicked and characterized by single-crystal X-ray diffraction (XRD). The bulk material was ground using a mortar and pestle and the powder was characterized by powder-XRD. The powder-XRD pattern had low intensity peaks of In_7Cl_9 and $PbCl_2$ impurities, but matched closely with the $InPb_2Cl_5$ phase. When $InPb_2Cl_5$ was left in ambient conditions over four months, the bulk absorbed moisture over time and left a light-grey film around the bulk with moisture build up on the side of the material.

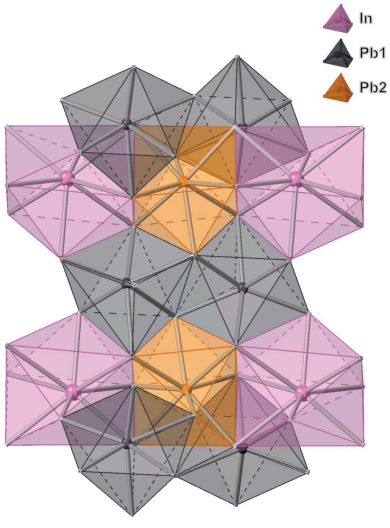

Table 1
Bond lengths (Å) in the $InPb_2Cl_5$ asymmetric unit (Fig. 1).

Bond	Distance
Cl1—Pb1	2.8677 (12)
Cl2—Pb1	2.9214 (10)
Cl3—Pb1	2.8744 (12)
Cl3—Pb2	2.9156 (12)
Cl4—Pb2	2.9236 (11)
Cl5—Pb2	2.9760 (12)

2. Structural commentary

The single-crystal structure of $InPb_2Cl_5$ was found to adopt a monoclinic $P2_1/c$ space group. The single-crystal structure refinement confirmed the composition as $InPb_2Cl_5$. The bond lengths in the asymmetric unit (Fig. 1) of $InPb_2Cl_5$ are listed in Table 1. The unit cell of $InPb_2Cl_5$ (Fig. 2) has four symmetry-related formula units. The Pb atoms in the unit cell (Fig. 2) coordinate multiple chlorine atoms that give a range of bond lengths from 2.868 (5)–3.3145 (15) Å. The Pb1 atoms coordinate with seven chlorine atoms in the structure, with bond lengths ranging from 2.868 (5)–3.1371 (14) Å. The Pb1 atoms form a nine-face polyhedron with a volume of 37.374 $Å^3$ (Fig. 3). The Pb2 atoms have a coordination number of 8 with bond lengths from 2.916 (7)–3.3145 (15) Å. The Pb2 atoms form a 12-face dodecahedron with a volume of 49.796 $Å^3$ (Fig. 3). The shortest bond length is between Cl1 and Pb1, which is 2.868 (5) Å. The largest bond lengths are between the Pb2 atom and a Cl3 atom at 3.3145 (15) Å. The typical bond length between Pb and Cl atoms is 2.44 Å in the binary structure. There is an increase in bond lengths from the binary $PbCl_2$ to the $InPb_2Cl_5$ structure. The indium atom interstitially coordinates eight chlorine atoms in a distorted octahedral geometry. The range of indium–chlorine bonds range from 3.1447 (18)–3.588 (8) Å. The indium atom forms a 12-face dodecahedron with a volume of 62.568 $Å^3$ (Fig. 3). The typical In—Cl bond length is around 2.56 Å, indicating that the indium–chlorine bonds have a much weaker interaction in the $InPb_2Cl_5$ structure. The largest bond angles seen in the unit cell (Fig. 2) are between the $Cl1^{iii}$—Pb1—Cl2 atoms at 156.02 (3)° (symmetry codes as per Fig. 2). The shortest bond angle in the structure is between the $Cl4^{ii}$—In1—$Cl5^{i}$ atoms at 63.2587 (3)°. The Pb atoms have stronger interactions with the chlorine atoms resulting in shorter bond lengths and a wide range of bond lengths from 69.7087 (3)–156.02 (3)°. The indium atoms have weaker interactions and are interstitially located throughout the structure. The weaker interactions of the indium atoms is evident because of the shorter bond lengths and smaller range of bond angles from 63.2587 (3)–144.1653 (3)°. A complete list of bond lengths and bond angles is given in the supporting information.

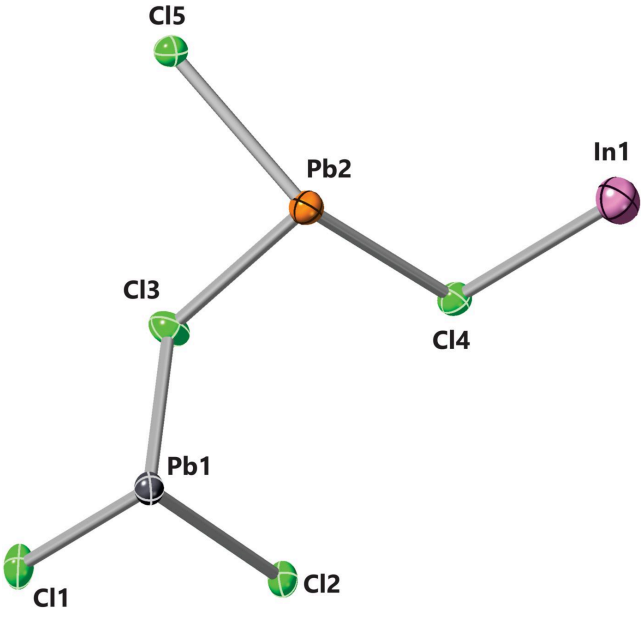

Figure 1
A view of the asymmetric unit. Ellipsoids are drawn at the 50% probability level.

Table 2
$InPb_2Cl_5$ unit-cell parameters compared with isostructural compounds..

Compound	a (Å)	b (Å)	c (Å)	β (°)	Volume ($Å^3$)
$InPb_2Cl_5$	8.9681 (11)	7.9033 (9)	12.4980 (16)	90.254 (6)	885.82 (19)
$TlPb_2Cl_5$	8.9561	7.9204	12.4908	90.073	886.0
$RbPb_2Cl_5$	8.9900	7.9963	12.541	90.20	901.5
KPb_2Cl_5	8.864	7.932	12.491	90.153	878.2

3. Database survey

The $InPb_2Cl_5$ structure is isostructural with other compounds such as $RbPb_2Cl_5$ (Isaenko *et al.*, 2013; Isaenko *et al.*, 2009),

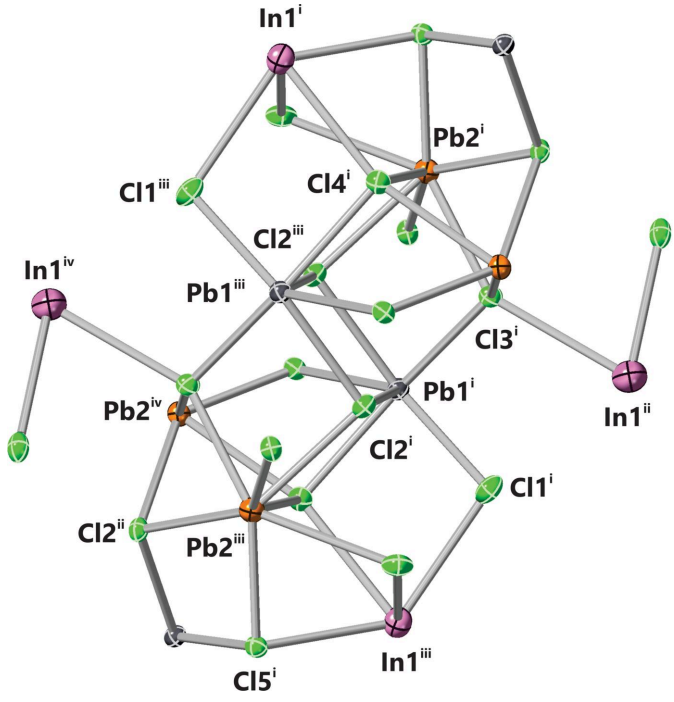

Figure 2
A partial packing plot viewed down the *b*-axis. Ellipsoids are drawn at the 50% probability level. Symmetry codes: (i) x, y, z; (ii) $-x, y+\frac{1}{2}, -z+\frac{1}{2}$; (iii) $-x, -y, -z$; (iv) $x, -y-\frac{1}{2}, z-\frac{1}{2}$.

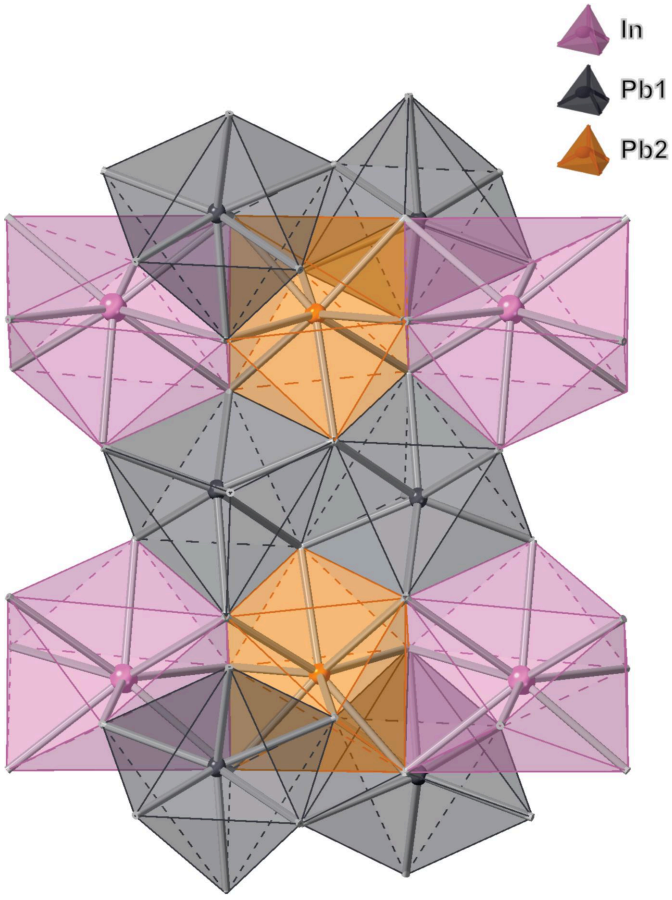

Figure 3
A polyhedron view of the crystal structure packing, viewed down the *b*-axis.

KPb_2Cl_5 (Rowe *et al.*, 2014; Isaenko *et al.*, 2009) and $TlPb_2Cl_5$ (Khyzhun *et al.*, 2014). The cell dimensions of the monoclinic $InPb_2Cl_5$ cell are compared with the isostructural compounds in Table 2. The cell dimensions for $InPb_2Cl_5$ match very closely with $TlPb_2Cl_5$. There is no significant difference between the $InPb_2Cl_5$ structure and the isostructural structures in Table 2, the small difference is due to the atomic size difference for indium. The indium atom has the smallest atom size, so it is expected to fit tighter into the unit cell compared to the other structures, so we see that $InPb_2Cl_5$ has the smallest unit cell volume. The thallium atom is most comparable to the indium atom size, which is why its cell dimensions are most similar.

4. Synthesis and crystallization

Stoichiometric amounts of the binary compounds $In^{I}Cl$ (4g, ThermoFisher Scientific 99.995%, metals basis) and $Pb^{II}Cl_2$ [3.7278 (5)g, Acros Organics 99%] were mixed in a glove box under an argon environment (<0.1ppm O_2 and H_2O). The binary compounds were ground together with a mortar and pestle and then loaded into a quartz ampoule. The quartz ampoule was flame sealed under high vacuum (5.5×10^{-5} mbar). The loaded quartz ampoule was heated at 3K min^{-1} in a vertical furnace to 793K. The ampoule was cooled at 0.5 K min^{-1} to room temperature. A 1 mm^3 piece of the metallic black and grey crystal was separated from the excess yellow $Pb^{II}Cl_2$ crystals and sent for characterization by powder-XRD and single-crystal XRD.

Table 3
Experimental details.

Crystal data	
Chemical formula	$In_2Pb_4Cl_{10}$
M_r	1412.9
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	298
a, b, c (Å)	8.9681 (11), 7.9033 (9), 12.4980 (16)
β (°)	90.254 (6)
V (Å^3)	885.82 (19)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	41.91
Crystal size (mm)	0.22 × 0.18 × 0.13
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (*SADABS*; Krause *et al.*, 2015)
T_{min}, T_{max}	0.378, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	20682, 2699, 2423
R_{int}	0.051
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.715
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.021, 0.042, 1.08
No. of reflections	2699
No. of parameters	74
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.22, −1.13

Computer programs: *APEX2* and *SAINT* (Bruker, 2012), *SHELXT* (Sheldrick, 2015*a*), *SHELXL* (Sheldrick, 2015*b*), *CrystalMaker* (Palmer, 2014), *WinGX* (Farrugia, 2012) and *publCIF* (Westrip, 2010).

5. Refinement

The crystallographic data, data collection and structure refinement are summarized in Table 3.

Acknowledgements

The authors would like to thank Queen's University and the Arthur B. Macdonald Institute for funding.

Funding information

Funding for this research was provided by: Natural Sciences and Engineering Research Council of Canada; Canada Foundation for Innovation; Canada First Research Excellence Fund.

References

Brown, E., Hanley, C. B., Hömmerich, U., Bluiett, A. G. & Trivedi, S. B. (2013). *J. Lumin.* **133**, 244–248.
Bruker (2012). *APEX2* and *SAINT*. Bruker AXS Inc, Madison, Wisconsin, USA.
Farrugia, L. J. (2012). *J. Appl. Cryst.* **45**, 849–854.

Isaenko, L. I., Merkulov, A. A., Tarasova, A. Yu., Pashkov, V. M. & Drebushchak, V. A. (2009). *J. Therm. Anal. Calorim.* **95**, 323–325.

Isaenko, L. I., Ogorodnikov, I. N., Pustovarov, V. A., Tarasova, A. Yu. & Pashkov, V. M. (2013). *Opt. Mater.* **35**, 620–625.

Khan, S., Mehmood, N., Ahmad, R., Kalsoom, A. & Hameed, K. (2022). *Mater. Sci. Semicond. Process.* **150**, 106973.

Khyzhun, O. Y., Bekenev, V. L., Denysyuk, N. M., Parasyuk, O. V. & Fedorchuk, A. O. (2014). *J. Alloys Compd.* **582**, 802–809.

Krause, L., Herbst-Irmer, R., Sheldrick, G. M. & Stalke, D. (2015). *J. Appl. Cryst.* **48**, 3–10.

Palmer, D. C. (2014). *CrystalMaker*. CrystalMaker Software Ltd, Begbroke, Oxfordshire, England.

Rowe, E., Tupitsyn, E., Bhattacharya, P., Matei, L., Groza, M., Buliga, V., Atkinson, G. & Burger, A. (2014). *J. Cryst. Growth*, **393**, 156–158.

Sheldrick, G. M. (2015*a*). *Acta Cryst.* A**71**, 3–8.

Sheldrick, G. M. (2015*b*). *Acta Cryst.* C**71**, 3–8.

Vu, T. V., Lavrentyev, A. A., Gabrelian, B. V., Vo, D. D., Pham, K. D., Denysyuk, N. M., Isaenko, L. I., Tarasova, A. Y. & Khyzhun, O. Y. (2020). *Opt. Mater.* **102**, 109793.

Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.

supporting information

Acta Cryst. (2023). E**79**, 942-945 [https://doi.org/10.1107/S2056989023007892]

Growth and characterization of a new inorganic metal–halide crystal structure, $InPb_2Cl_5$

Michael P. Lewis, Ramjee Kandel, Gabriele Schatte and Peng L. Wang

Computing details

Cell refinement: *APEX2* (Bruker, 2012); data reduction: *SAINT* (Bruker, 2012); program(s) used to solve structure: *SHELXT* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL* (Sheldrick, 2015b); molecular graphics: *CrystalMaker* (Palmer, 2014); software used to prepare material for publication: *WinGX* (Farrugia, 2012) and *publCIF* (Westrip, 2010).

Indium dilead pentachloride

Crystal data

$In_2Pb_4Cl_{10}$
M_r = 1412.9
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
a = 8.9681 (11) Å
b = 7.9033 (9) Å
c = 12.4980 (16) Å
β = 90.254 (6)°
V = 885.82 (19) Å^3
Z = 2
$F(000)$ = 1192
D_x = 5.297 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 9997 reflections
θ = 2.3–30.5°
μ = 41.91 mm^{-1}
T = 298 K
Transparent square, colourless
0.22 × 0.18 × 0.13 mm

Data collection

Bruker APEXII CCD diffractometer
Radiation source: sealed X-ray tube, Incoatec Iμs
Graphite monochromator
Detector resolution: 7.9 pixels mm^{-1}
φ and ω scans
Absorption correction: multi-scan (SADABS; Krause *et al.*, 2015)
T_{min} = 0.378, T_{max} = 0.746
20682 measured reflections
2699 independent reflections
2423 reflections with $I > 2\sigma(I)$
R_{int} = 0.051
θ_{max} = 30.6°, θ_{min} = 2.3°
h = −12→12
k = −11→11
l = −17→17

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.021
$wR(F^2)$ = 0.042
S = 1.08
2699 reflections
74 parameters
0 restraints
0 constraints
Primary atom site location: structure-invariant direct methods
$w = 1/[\sigma^2(F_o^2) + (0.0083P)^2 + 1.8133P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.002
$\Delta\rho_{max}$ = 1.22 e Å^{-3}
$\Delta\rho_{min}$ = −1.13 e Å^{-3}

Extinction correction: SHELXL-2018/3 (Sheldrick 2015b), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.00232 (8)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Cl1	0.04109 (12)	0.67574 (15)	0.41739 (11)	0.0316 (3)
Cl2	0.45758 (11)	0.66555 (13)	0.40434 (9)	0.0226 (2)
Cl3	0.27835 (14)	0.65746 (14)	0.68735 (10)	0.0304 (3)
Cl4	0.72918 (12)	0.68702 (14)	0.72264 (9)	0.0252 (2)
Cl5	0.28105 (12)	0.45943 (14)	1.00167 (9)	0.0232 (2)
In1	0.98678 (5)	0.45346 (6)	0.83468 (4)	0.04410 (11)
Pb1	0.24664 (2)	0.43551 (2)	0.50647 (2)	0.02229 (6)
Pb2	0.49498 (2)	0.48805 (2)	0.82509 (2)	0.02538 (6)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0194 (5)	0.0309 (6)	0.0445 (7)	0.0009 (4)	0.0017 (5)	0.0137 (5)
Cl2	0.0192 (5)	0.0201 (4)	0.0285 (6)	−0.0008 (4)	−0.0002 (4)	0.0059 (4)
Cl3	0.0364 (6)	0.0283 (5)	0.0263 (6)	0.0084 (5)	−0.0081 (5)	−0.0063 (4)
Cl4	0.0259 (5)	0.0254 (5)	0.0243 (6)	−0.0027 (4)	0.0021 (4)	0.0025 (4)
Cl5	0.0251 (5)	0.0240 (5)	0.0205 (5)	0.0004 (4)	0.0005 (4)	0.0009 (4)
In1	0.0418 (2)	0.0432 (2)	0.0472 (3)	0.00874 (18)	−0.00359 (19)	−0.00495 (19)
Pb1	0.01876 (9)	0.02412 (9)	0.02399 (10)	−0.00042 (6)	−0.00025 (6)	−0.00142 (6)
Pb2	0.02614 (10)	0.02526 (9)	0.02473 (10)	−0.00304 (7)	0.00037 (7)	0.00179 (6)

Geometric parameters (Å, º)

Cl1—Pb1	2.8677 (12)	Cl3—Pb2	2.9156 (12)
Cl1—Pb1^{i}	2.8912 (11)	Cl4—Pb2	2.9236 (11)
Cl2—Pb1	2.9214 (10)	Cl4—Pb1^{iii}	3.0314 (12)
Cl2—Pb2^{ii}	2.9311 (10)	Cl5—Pb2	2.9394 (11)
Cl2—Pb1^{iii}	2.9817 (11)	Cl5—Pb2^{iv}	2.9760 (12)
Cl3—Pb1	2.8744 (12)		
Pb1—Cl1—Pb1^{i}	104.12 (4)	Cl2—Pb1—Cl2^{iii}	75.72 (3)
Pb1—Cl2—Pb2^{ii}	143.53 (4)	Cl1—Pb1—Cl4^{iii}	83.88 (4)
Pb1—Cl2—Pb1^{iii}	104.28 (3)	Cl3—Pb1—Cl4^{iii}	158.52 (3)
Pb2^{ii}—Cl2—Pb1^{iii}	105.88 (3)	Cl1^{i}—Pb1—Cl4^{iii}	106.34 (4)
Pb1—Cl3—Pb2	104.33 (4)	Cl2—Pb1—Cl4^{iii}	74.75 (3)

Pb2—Cl4—Pb1^{iii}	107.24 (4)	Cl2^{iii}—Pb1—Cl4^{iii}	101.55 (3)
Pb2—Cl5—Pb2^{iv}	95.44 (3)	Cl3—Pb2—Cl4	88.42 (4)
Cl1—Pb1—Cl3	87.85 (4)	Cl3—Pb2—Cl2^{v}	72.16 (3)
Cl1—Pb1—Cl1^{i}	75.88 (4)	Cl4—Pb2—Cl2^{v}	74.28 (3)
Cl3—Pb1—Cl1^{i}	90.69 (4)	Cl3—Pb2—Cl5	92.48 (3)
Cl1—Pb1—Cl2	80.49 (3)	Cl4—Pb2—Cl5	147.44 (3)
Cl3—Pb1—Cl2	84.37 (4)	Cl2^{v}—Pb2—Cl5	75.06 (3)
Cl1^{i}—Pb1—Cl2	156.02 (3)	Cl3—Pb2—Cl5^{iv}	144.23 (3)
Cl1—Pb1—Cl2^{iii}	153.09 (3)	Cl4—Pb2—Cl5^{iv}	76.10 (3)
Cl3—Pb1—Cl2^{iii}	77.57 (3)	Cl2^{v}—Pb2—Cl5^{iv}	72.65 (3)
Cl1^{i}—Pb1—Cl2^{iii}	126.11 (3)	Cl5—Pb2—Cl5^{iv}	84.56 (3)

Symmetry codes: (i) −*x*, −*y*+1, −*z*+1; (ii) *x*, −*y*+3/2, *z*−1/2; (iii) −*x*+1, −*y*+1, −*z*+1; (iv) −*x*+1, −*y*+1, −*z*+2; (v) *x*, −*y*+3/2, *z*+1/2.