Acta Crystallographica Section E
Structure Reports
Online

ISSN 1600-5368

Dilead(II) chromium(III) heptafluoride

Armel Le Bail

Université du Maine, Laboratoire des Oxydes et Fluorures, CNRS UMR 6010, Avenue O. Messiaen,72085 Le Mans, France
Correspondence e-mail: armel.le_bail@univ-lemans.fr

Received 18 March 2010; accepted 26 March 2010

Key indicators: single-crystal X-ray study; T = 293 K; mean σ(Pb–F) = 0.006 Å; R factor = 0.036; wR factor = 0.084; data-to-parameter ratio = 26.9.

Single crystals of the title compound, Pb_2CrF_7, were obtained by solid-state reaction. The monoclinic structure is isotypic with Pb_2RhF_7 and is built up of CrF_6^{3-} octahedra isolated from each other, inserted in a fluorite-related matrix of PbF_6 distorted octahedra, and PbF_8 square antiprisms sharing edges and corners. The seventh F atom is 'independent', connected only to three Pb atoms within FPb_3 triangles, sharing an edge and building an almost planar Pb_4F_2 unit, so that the formula can alternatively be written as $Pb_2F(CrF_6)$.

Related literature

For the Pb_2RhF_7 structure-type, see: Domesle & Hoppe (1983), and for isostructural Sr_2RhF_7, see: Grosse & Hoppe (1987). For the indexed powder pattern of Pb_2CrF_7, see: de Kozak *et al.* (1999). For other compounds containing 'independent' fluorine atoms coordinated to three cations (Ca or Sr) in a plane, see: Ca_2AlF_7 (Domesle & Hoppe, 1980); $Sr_5Zr_3F_{22}$ (Le Bail, 1996); $Sr_5(VOF_5)_3F(H_2O)_3$ (Le Bail *et al.*, 2009). For fluorite-related lead-based compounds, see: $Pb_8MnFe_2F_{24}$ (Le Bail & Mercier, 1992); Pb_2ZrF_8 (Le Bail & Laval, 1998). For the structure simulation of fluoride glasses containing lead by using crystalline models, see: Le Bail (1989, 2000). For details and parameters of the bond-valence model, see: Brown & Altermatt (1985); Brese & O'Keeffe (1991).

Experimental

Crystal data

Pb_2CrF_7
M_r = 599.40
Monoclinic, $P2_1/c$
a = 5.4626 (7) Å
b = 11.2085 (15) Å
c = 9.5738 (11) Å
β = 91.197 (10)°
V = 586.05 (13) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 59.61 mm^{-1}
T = 293 K
0.12 × 0.07 × 0.01 mm

Data collection

Siemens AED2 diffractometer
Absorption correction: Gaussian (*SHELX76*; Sheldrick, 2008)
T_{min} = 0.011, T_{max} = 0.321
6770 measured reflections
2506 independent reflections
2082 reflections with $I > 2\sigma(I)$
R_{int} = 0.041
3 standard reflections every 120 min
intensity decay: 15%

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.036
$wR(F^2)$ = 0.084
S = 1.64
2506 reflections
93 parameters
$\Delta\rho_{max}$ = 3.17 e Å^{-3}
$\Delta\rho_{min}$ = −2.20 e Å^{-3}

Table 1
Selected bond lengths (Å).

Pb1—F1	2.324 (5)	Pb2—F2^{iv}	2.586 (5)
Pb1—F7^{i}	2.437 (5)	Pb2—F6	2.632 (6)
Pb1—F4^{ii}	2.439 (5)	Pb2—F3^{iv}	2.653 (5)
Pb1—F5^{iii}	2.620 (6)	Pb2—F7	2.743 (6)
Pb1—F6^{iv}	2.640 (7)	Cr—F2	1.883 (5)
Pb1—F2^{v}	2.899 (6)	Cr—F3	1.900 (5)
Pb1—F6^{v}	3.067 (7)	Cr—F4	1.907 (5)
Pb2—F1	2.412 (5)	Cr—F5	1.909 (5)
Pb2—F1^{ii}	2.441 (4)	Cr—F6	1.912 (6)
Pb2—F5^{i}	2.497 (6)	Cr—F7	1.931 (4)
Pb2—F3^{vi}	2.512 (6)		

Symmetry codes: (i) $-x, y+\frac{1}{2}, -z+\frac{1}{2}$; (ii) $-x, -y+1, -z$; (iii) $x, y+1, z$; (iv) $-x+1, y+\frac{1}{2}, -z+\frac{1}{2}$; (v) $-x+1, -y+1, -z$; (vi) $x, -y+\frac{1}{2}, z-\frac{1}{2}$.

Table 2
Valence-bond analysis according to the empirical expression from Brown & Altermatt (1985), using parameters for solids from Brese & O'Keeffe (1991), with two results for Pb1 and Pb2 according to their coordinations (respectively VI or XI, and VIII or IX).

	Cr	Pb1	Pb2	Σ	Σexpected
F1		0.45	0.36 + 0.33	1.14	1
F2	0.52	0.10 + 0.05	0.22	0.89	1
F3	0.50	0.04	0.27 + 0.19	1.00	1
F4	0.49	0.33 + 0.04	0.05	0.91	1
F5	0.48	0.20	0.28	0.96	1
F6	0.48	0.19 + 0.06	0.20	0.93	1
F7	0.46	0.33 + 0.03	0.15	0.97	1
Σ	2.93	1.60 (VI)	2.00 (VIII)		
or		1.82 (XI)	2.05 (IX)		
Σexpected	3	2	2		

Table 3
Comparison of the cell parameters of the three isostructural heptafluorides showing a noticeable anomaly on the c parameter of the chromium compound.

Formula	a	b	c	β	V
$Pb_2RhF_7{}^a$	5.569	11.854	8.832	91.00	582.96
$Sr_2RhF_7{}^b$	5.510	11.628	8.640	90.98	553.49
$Pb_2CrF_7{}^c$	5.463	11.208	9.574	91.20	586.05

Notes: (a) Domesle & Hoppe (1983); (b) Grosse & Hoppe (1987); (c) this work.

Data collection: *STADI4* (Stoe & Cie, 1998); cell refinement: *STADI4*; data reduction: *X-RED* (Stoe & Cie, 1998); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 2005) and *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *publCIF* (Westrip, 2010).

Thanks are due to Professor M. Leblanc for the X-ray data recording and to A.-M. Mercier for the solid-state synthesis.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: WM2317).

References

Brandenburg, K. (2005). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.
Brese, N. E. & O'Keeffe, M. (1991). *Acta Cryst.* B**47**, 192–197.
Brown, I. D. & Altermatt, D. (1985). *Acta Cryst.* B**41**, 244–247.
Domesle, R. & Hoppe, R. (1980). *Z. Kristallogr.* **153**, 317–328.
Domesle, R. & Hoppe, R. (1983). *Z. Anorg. Allg. Chem.* **501**, 102–110.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Grosse, L. & Hoppe, R. (1987). *Z. Anorg. Allg. Chem.* **552**, 123–131.
Kozak, A. de (1999). ICDD PDF card 00-051-0237.
Le Bail, A. (1989). *J. Solid State Chem.* **83**, 267–271.
Le Bail, A. (1996). *Eur. J. Solid State Inorg. Chem.* **33**, 1211–1222.
Le Bail, A. (2000). *J. Non-Cryst. Solids* **271**, 249–259.
Le Bail, A. & Laval, J.-P. (1998). *Eur. J. Solid State Inorg. Chem.* **35**, 357–372.
Le Bail, A. & Mercier, A.-M. (1992). *Eur. J. Solid State Inorg. Chem.* **29**, 183–190.
Le Bail, A., Mercier, A.-M. & Dix, I. (2009). *Acta Cryst.* E**65**, i46–i47.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Stoe & Cie (1998). *STADI4* and *X-RED*. Stoe & Cie, Darmstadt, Germany.
Westrip, S. P. (2010). *publCIF*. In preparation.

supplementary materials

Acta Cryst. (2010). E**66**, i32-i33 [**doi:10.1107/S1600536810011608**]

Dilead(II) chromium(III) heptafluoride

A. Le Bail

Comment

Continuing investigations of crystalline complex compounds of lead and 3*d* metal cation fluorides having chemical formulations similar to some fluoride glasses for structure modelling purposes (Le Bail, 2000), such as $Pb_8MnFe_2F_{24}$ (Le Bail & Mercier, 1992) or $NaPbFe_2F_9$ (Le Bail, 1989), the title compound, Pb_2CrF_7, was synthesized and characterized from single crystal X-ray data. The results confirm that it is isostructural with Pb_2RhF_7 (Domesle & Hoppe, 1983), as mentioned previously by de Kozak *et al.* (1999). The monoclinic structure is built up of CrF_6^{3-} octahedra (Fig. 1) isolated from each other, inserted in a fluorite-related matrix of PbF_6 distorted octahedra and PbF_8 square antiprisms sharing edges and corners. The seventh fluorine atom is "independent", connected only to 3 Pb atoms in FPb_3 triangles, sharing an edge and building an almost planar Pb_4F_2 unit (Fig. 2), so that the formula can be alternatively written as $Pb_2F(CrF_6)$. There are some differences observed with the Pb_2RhF_7 structure-type. The Pb1 atom appears to be six-coordinated in Pb_2CrF_7 with Pb—F distances ranging from 2.324 (5) to 2.899 (6) Å, there are then 5 next F atoms being between 3.067 (7) and 3.364 (6) Å whereas in Pb_2RhF_7, Pb1 looks eightfold coordinated (Pb—F distances between 2.375 and 2.744 Å), with two next F atoms at 3.105 and 3.219 Å. The bond valence calculations show that the first 6 F atoms around Pb1 cannot really satisfy the Pb^{2+} charge and that the 5 next F atoms contribute to the overall bond valence (Table 2). The behaviour of the cell parameters is surprising in the series of the three isostructural compounds. If all cell parameters are logically smaller in Sr_2RhF_7 (Grosse & Hoppe, 1987) than in Pb_2RhF_7, due to the smaller Sr^{2+} size, in Pb_2CrF_7 one observes that only *a* and *b* are smaller but that *c* is much larger, in spite of the Cr^{3+} cation being smaller than Rh^{3+} (Table 3). Finally, the cell volume of Pb_2CrF_7 is even slightly larger than that of Pb_2RhF_7.

Usually, such fluorinated phases with high A^{II}/M ratio (A^{II} = Ca, Pb, Sr ; *M* = 3*d* element or In, Nb, Zr, etc), are found to be related to the fluorite structure adopted by PbF_2 or SrF_2. The relation is in general easy to establish due to the presence of "independent" F atoms (not bonded to *M*) which are found to form characteristic FPb_4 tetrahedra. But this is not obvious here (Fig. 3) since no such FPb_4 tetrahedron is observed. Other compounds containing "independent" fluorine atoms coordinated to three cations (Ca or Sr) in a plane are Ca_2AlF_7 (Domesle & Hoppe, 1980), $Sr_5Zr_3F_{22}$ (Le Bail, 1996) and $Sr_5(VOF_5)_3F(H_2O)_3$ (Le Bail *et al.*, 2009), the last two being strongly related to the fluorite structure in which the FSr_3 triangles were found to interconnect the fluorite-related blocks. An examination of the Pb coordinates in Pb_2CrF_7 along the *a* axis (which is close to the PbF_2 fluorite cell parameter) shows that they alternate at values *x*~1/4 and 3/4, forming fluorite-related strips corrugating in the *ac* plane where highly distorted PbF_8 cubes as expected in the fluorite structure were obtained by small displacements of some of the F atoms as evidenced in Fig. 4 . Similar corrugated strips were observed for the Pb_2ZrF_8 structure (Le Bail & Laval, 1998), where the Zr^{4+} cations occupy bicapped trigonal prisms at positions similar to those of Cr^{3+} in the title compound. In Pb_2ZrF_8, the Pb^{2+} lone pair position was suggested by comparison of the Pb coordination with that of Ba in the isostructural α-Ba_2ZrF_8 structure, observing some strong distorsions, the stereochemically active lone pair repelling clearly some F atoms. The same exercice is not so obvious here, even by comparing Sr_2RhF_7 with Pb_2RhF_7. However, there is a specific pattern of differences in the bond lengths (3 adjacent short Pb—F bonds and 3 adjacent long ones for Pb1; 4 short and 4 long for Pb2) which could be attributed to repulsion effects involving a somehow weak stereochemically active lone pair producing the longer Pb—F distances. The Pb1 lone pair is thus probably oriented towards the barycenter of the (F5—F6—F2) face of the $Pb1F_6$ octahedron, a similar reasoning applying to the Pb2 lone pair.

Experimental

Solid state reaction between $2PbF_2$ and CrF_3 at 773 K for 96 hours in a platinum tube sealed under argon yieded single crystal of the title compound.

Refinement

The highest residual peak and deepest hole in the final difference map were located respectively 0.67 Å and 0.83 Å from the Pb2 atom.

Figures

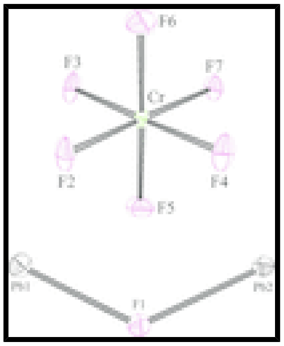

Fig. 1. *ORTEP-3* view (Farrugia, 1997) of the regular $[Cr^{III}F_6]^{3-}$ octahedron and of the "independent" fluoride ion F1 connected to Pb1 and Pb2 completing the $Pb_2F(CrF_6)$ formula (ellipsoids at the 50% probability level).

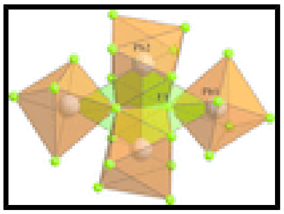

Fig. 2. Diamond (Brandenburg, 2005) view of the two $F1Pb_3$ triangles sharing an edge in order to form the planar F_2Pb_4 unit with $Pb1F_6$ distorted octahedra and $Pb2F_8$ square antiprisms.

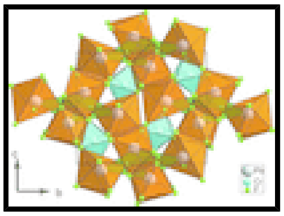

Fig. 3. Diamond (Brandenburg, 2005) view of the crystal packing along [100] showing the isolated $[CrF_6]$ octahedra,

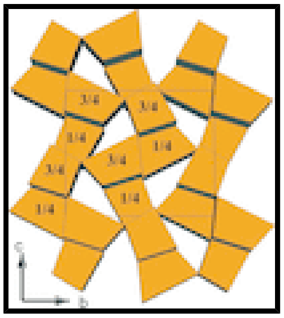

Fig. 4. Idealized (with small displacement of some F atoms) view of the Pb atoms alternating positions close to $x = 1/4$ and 3/4, building corrugated strips with the PbF_2 fluorite structure. Similar kinked blocks were observed for Pb_2ZrF_8 (Le Bail & Laval, 1998).

Dilead(II) chromium(III) heptafluoride

Crystal data

Pb_2CrF_7

$M_r = 599.40$

Monoclinic, $P2_1/c$

Hall symbol: -P 2ybc

$a = 5.4626$ (7) Å

$b = 11.2085$ (15) Å

$c = 9.5738$ (11) Å

$\beta = 91.197$ (10)°

$V = 586.05$ (13) Å^3

$Z = 4$

$F(000) = 1004$

$D_x = 6.793$ Mg m^{-3}

Mo $K\alpha$ radiation, $\lambda = 0.71069$ Å

Cell parameters from 40 reflections

$\theta = 2.8$–35°

$\mu = 59.61$ mm^{-1}

$T = 293$ K

Platelet, green

0.12 × 0.07 × 0.01 mm

Data collection

Siemens AED2 diffractometer

Radiation source: fine-focus sealed tube

graphite

$2\theta/\omega$ scans

Absorption correction: gaussian (SHELX76; Sheldrick, 2008)

$T_{min} = 0.011$, $T_{max} = 0.321$

6770 measured reflections

2506 independent reflections

2082 reflections with $I > 2\sigma(I)$

$R_{int} = 0.041$

$\theta_{max} = 35.0°$, $\theta_{min} = 2.8°$

$h = -8 \rightarrow 8$

$k = 0 \rightarrow 18$

$l = 0 \rightarrow 15$

3 standard reflections every 120 min

intensity decay: 15%

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.036$

$wR(F^2) = 0.084$

$S = 1.64$

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

$w = [\exp(2.00(\sin\theta/\lambda)^2)]/[\sigma^2(F_o^2) + (0.0528P)^2]$

where $P = 0.33333F_o^2 + 0.66667F_c^2$

$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 3.17$ e Å^{-3}

2506 reflections	$\Delta\rho_{\min} = -2.20$ e Å^{-3}
93 parameters	Extinction correction: SHELXL97 (Sheldrick, 2008), $Fc^{*}=kFc[1+0.001xFc^{2}\lambda^{3}/\sin(2\theta)]^{-1/4}$
0 restraints	Extinction coefficient: 0.0171 (7)
0 constraints	

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.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}
Pb1	0.21926 (4)	0.81248 (3)	0.05527 (3)	0.01669 (9)
Pb2	0.23992 (4)	0.43908 (2)	0.13531 (3)	0.01410 (9)
Cr	0.30002 (17)	0.13284 (9)	0.20773 (11)	0.01105 (17)
F1	0.1204 (9)	0.6150 (4)	0.0059 (6)	0.0212 (9)
F2	0.5511 (9)	0.0321 (5)	0.1456 (6)	0.0240 (10)
F3	0.3978 (9)	0.0941 (5)	0.3938 (6)	0.0233 (10)
F4	0.2089 (10)	0.1752 (6)	0.0208 (6)	0.0253 (10)
F5	0.0826 (9)	−0.0003 (5)	0.1978 (7)	0.0251 (11)
F6	0.5281 (10)	0.2622 (6)	0.2141 (8)	0.0307 (13)
F7	0.0430 (8)	0.2415 (5)	0.2594 (5)	0.0190 (8)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Pb1	0.01615 (12)	0.01664 (12)	0.01736 (14)	−0.00212 (8)	0.00190 (8)	−0.00028 (8)
Pb2	0.01326 (11)	0.01521 (11)	0.01376 (12)	−0.00018 (7)	−0.00137 (7)	0.00039 (8)
Cr	0.0087 (3)	0.0131 (4)	0.0113 (4)	0.0010 (3)	0.0002 (3)	0.0013 (3)
F1	0.0202 (18)	0.0153 (17)	0.028 (3)	−0.0008 (16)	−0.0086 (17)	0.0004 (17)
F2	0.023 (2)	0.032 (2)	0.018 (2)	0.0174 (19)	0.0007 (17)	−0.0013 (18)
F3	0.023 (2)	0.037 (3)	0.010 (2)	0.0123 (19)	−0.0022 (16)	0.0025 (17)
F4	0.026 (2)	0.039 (3)	0.011 (2)	0.010 (2)	0.0022 (17)	0.0067 (19)
F5	0.023 (2)	0.0195 (19)	0.033 (3)	−0.0058 (18)	0.001 (2)	−0.0061 (19)
F6	0.019 (2)	0.024 (2)	0.049 (4)	−0.0056 (19)	0.000 (2)	0.002 (2)
F7	0.0140 (16)	0.022 (2)	0.021 (2)	0.0084 (16)	0.0022 (15)	−0.0009 (16)

Geometric parameters (Å, °)

Pb1—F1	2.324 (5)	Cr—F4	1.907 (5)
Pb1—F7^{i}	2.437 (5)	Cr—F5	1.909 (5)
Pb1—F4^{ii}	2.439 (5)	Cr—F6	1.912 (6)
Pb1—F5^{iii}	2.620 (6)	Cr—F7	1.931 (4)
Pb1—F6^{iv}	2.640 (7)	F2—F3	2.630 (8)
Pb1—F2^{v}	2.899 (6)	F2—F5	2.643 (8)
Pb1—F6^{v}	3.067 (7)	F2—F6	2.665 (9)
Pb2—F1	2.412 (5)	F2—F4	2.721 (7)
Pb2—F1^{ii}	2.441 (4)	F3—F6	2.659 (9)
Pb2—F5^{i}	2.497 (6)	F3—F5	2.734 (8)
Pb2—F3^{vi}	2.512 (6)	F3—F7	2.835 (6)
Pb2—F2^{iv}	2.586 (5)	F4—F7	2.584 (8)
Pb2—F6	2.632 (6)	F4—F5	2.696 (8)
Pb2—F3^{iv}	2.653 (5)	F4—F6	2.698 (9)
Pb2—F7	2.743 (6)	F5—F7	2.784 (8)
Cr—F2	1.883 (5)	F6—F7	2.704 (7)
Cr—F3	1.900 (5)		
F2—Cr—F3	88.1 (2)	F4—Cr—F6	89.9 (3)
F2—Cr—F4	91.8 (2)	F5—Cr—F6	177.6 (3)
F3—Cr—F4	178.3 (3)	F2—Cr—F7	176.1 (2)
F2—Cr—F5	88.4 (3)	F3—Cr—F7	95.5 (2)
F3—Cr—F5	91.7 (3)	F4—Cr—F7	84.6 (2)
F4—Cr—F5	89.9 (3)	F5—Cr—F7	92.9 (2)
F2—Cr—F6	89.2 (3)	F6—Cr—F7	89.4 (3)
F3—Cr—F6	88.5 (3)		

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

Table 2
Valence-bond analysis according to the empirical expression from Brown & Altermatt (1985), using parameters for solids from Brese & O'Keeffe (1991), with two results for Pb1 and Pb2 according to their coordinations (respectively VI or XI, and VIII or IX).

	Cr	Pb1	Pb2	Σ	Σexpected
F1		0.45	0.36+0.33	1.14	1
F2	0.52	0.10+0.05	0.22	0.89	1
F3	0.50	0.04	0.27+0.19	1.00	1
F4	0.49	0.33+0.04	0.05	0.91	1
F5	0.48	0.20	0.28	0.96	1
F6	0.48	0.19+0.06	0.20	0.93	1
F7	0.46	0.33+0.03	0.15	0.97	1
Σ	2.93	1.60(VI)	2.00(VIII)		
or		1.82(XI)	2.05(IX)		
Σexpected	3	2	2		

Table 3

Comparison of the cell parameters of the three isostructural heptafluorides showing a noticeable anomaly on the c parameter of the chromium compound.

Formula	*a*	*b*	*c*	β	*V*
Pb_2RhF_7[a]	5.569	11.854	8.832	91.00	582.96
Sr_2RhF_7[b]	5.510	11.628	8.640	90.98	553.49
Pb_2CrF_7[c]	5.463	11.208	9.574	91.20	586.05

Notes: (*a*) Domesle & Hoppe (1983); (*b*) Grosse & Hoppe (1987); (*c*) this work.

Fig. 1

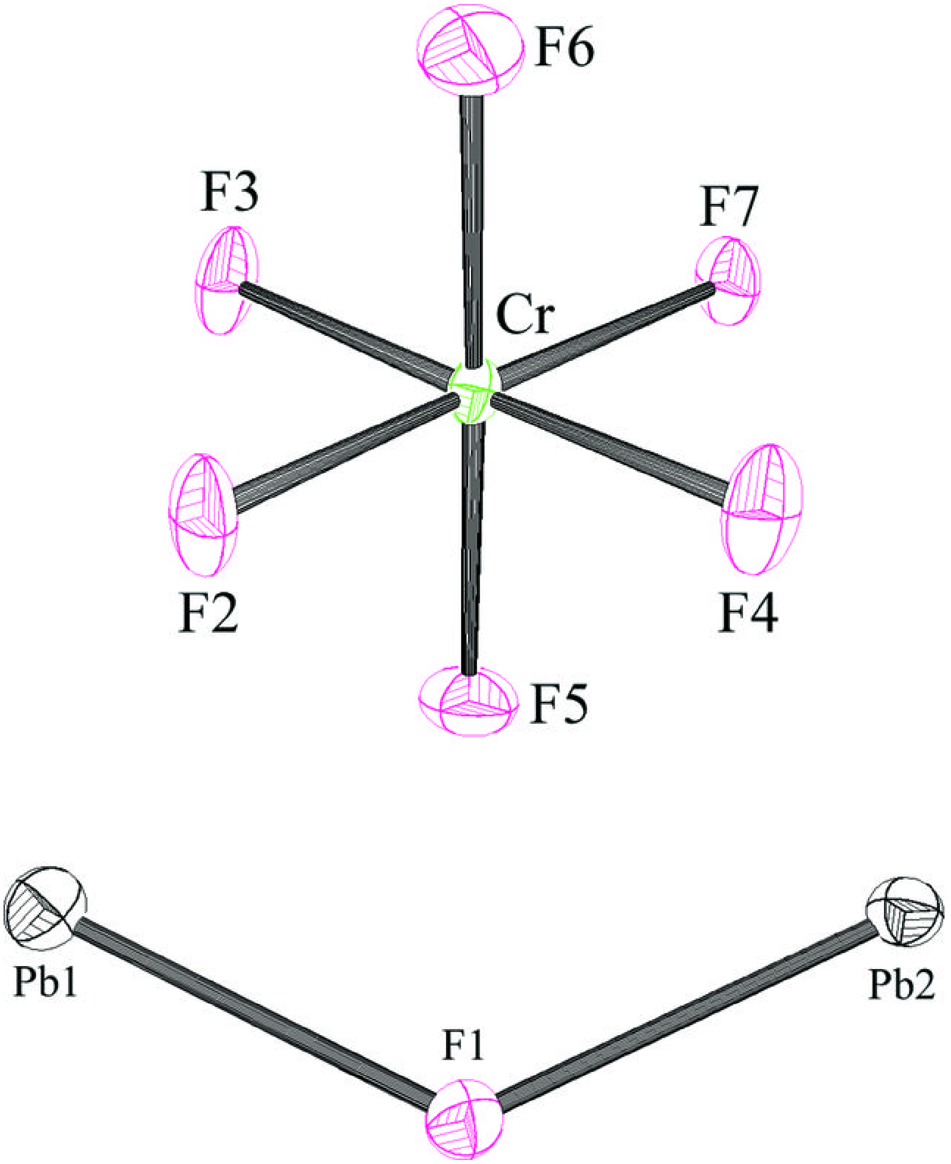

Fig. 2

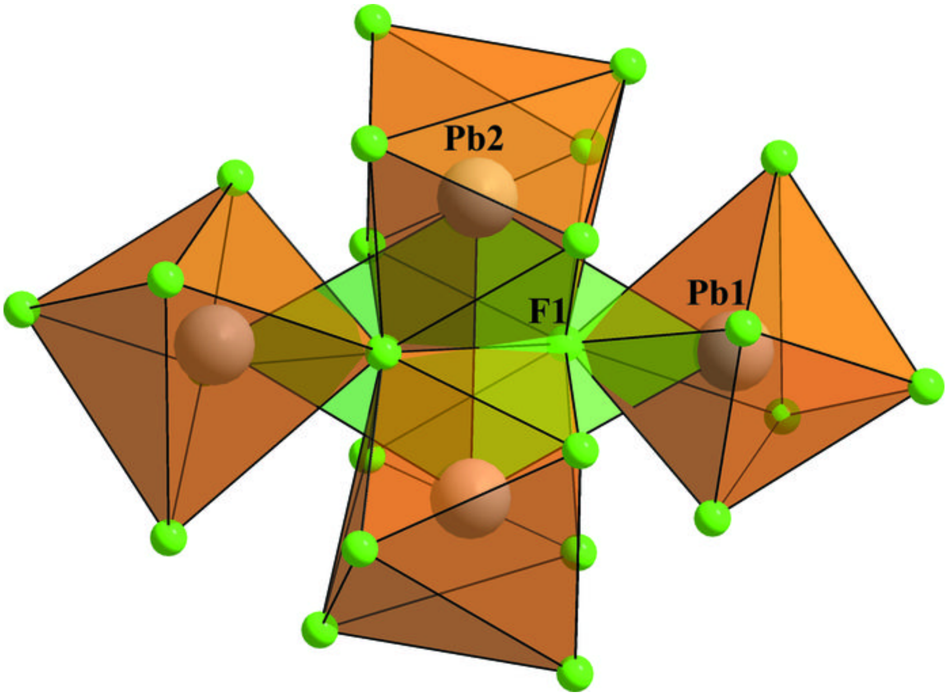

Fig. 3

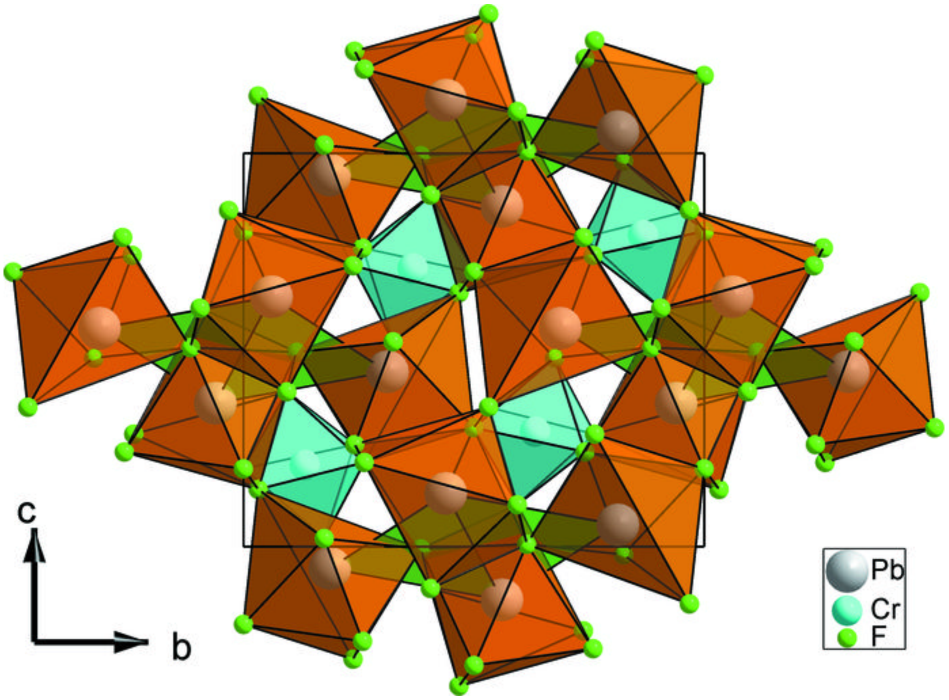

Fig. 4