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The ordered hydrocerussite-type structure of $(PbCO_3)_2{\cdot}BaF_2$

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Single crystals of synthetic $(PbCO_3)_2{\cdot}BaF_2$, bis[lead(II) carbonate] barium difluoride, have been grown under hydrothermal conditions. The compound crystallizes in the ordered hydrocerussite $[(PbCO_3)_2{\cdot}Pb(OH)_2]$ structure and can be derived from a close packing of the metal atoms with a stacking sequence of $[c(h)_2]_3$ along the c axis. O and F atoms are situated approximately in the tetrahedral voids, resulting in the formation of a slightly distorted $[BaF_6O_6]$ icosahedron and a [1+6+3]-coordinate Pb atom, with one short bond to F, six bonds to O and three longer bonds to additional O atoms. The carbonate group deviates only slightly from the geometry of an equilateral triangle.

Comment

In the course of experiments on the synthesis of compounds containing a matlockite-type [4+4+1] coordination of halogen atoms around the divalent metal, which are promising candidates for optical hole-burning or are suitable as host lattices for doping with rare earth ions to synthesize new luminescent materials, the phases $Ba_2Pb_4F_{10}Br_{2-x}I_x$ (x = 0–2) were prepared hydrothermally and characterized by single-crystal structure analysis (Weil & Kubel, 2000). Experiments to substitute Cl for Br or I, intended to prepare a new $Ba_2Pb_4F_{10}Cl_2$ phase, failed and crystals of composition $(PbCO_3)_2{\cdot}BaF_2$ were formed instead. Structure analysis of this phase revealed a metrical relationship (rhombohedral, unit cell with $a \simeq 5.2$ Å and $c \simeq 23.4$ Å in hexagonal setting) and a formula similar to the basic lead carbonate, $(PbCO_3)_2{\cdot}Pb(OH)_2$, also known as the mineral hydrocerussite. In its synthetic form, this compound is named 'white lead', a pigment with one of the highest opacities reported, and which has been used since ancient times (Soukup, 1999) and is still employed as a nacreous pigment (Morita, 1985; Franz *et al.*, 1992).

The structure of $(PbCO_3)_2{\cdot}BaF_2$ can be derived from a close packing of the metal atoms, with a stacking sequence of $[c(h)_2]_3$ along the c axis, according to the Jagodzinski notation (Jagodzinski, 1949; Verma & Krishna, 1966). In this sequence, two adjacent layers of Pb atoms, forming the h layers, are separated by a layer of Ba atoms, which represent the c layer (Fig. 1). This arrangement leads to a distorted [6+6] icosahedral coordination around the Ba atom, with six shorter bonds to the F atoms and six longer bonds to the corners of the carbonate groups (Fig. 2*a*). The Pb atom shows a [1+6+3] coordination, with one very short Pb—F bond to the vertex of the coordination polyhedron, six chelate-type bonds to the edges of three intra-layer CO_3 groups and three longer bonds to the corners of CO_3 groups of the adjacent layer (Fig. 2*b*). The F atoms are approximately situated in the tetrahedral voids of the close-packed arrangement, whereas the O and C atoms are considerably dislocated from the tetrahedral and octahedral voids, respectively. The F atom is surrounded by three Ba atoms and one Pb atom, forming a compressed tetrahedron with a mean angle of 108.6° (Fig. 2*c*). The O atom has a coordination number of 4, with bonds to two Pb atoms, one Ba atom and one C atom. The corresponding coordination polyhedron is a considerably distorted tetrahedron, with a mean angle of 110.6° (Fig. 2*d*).

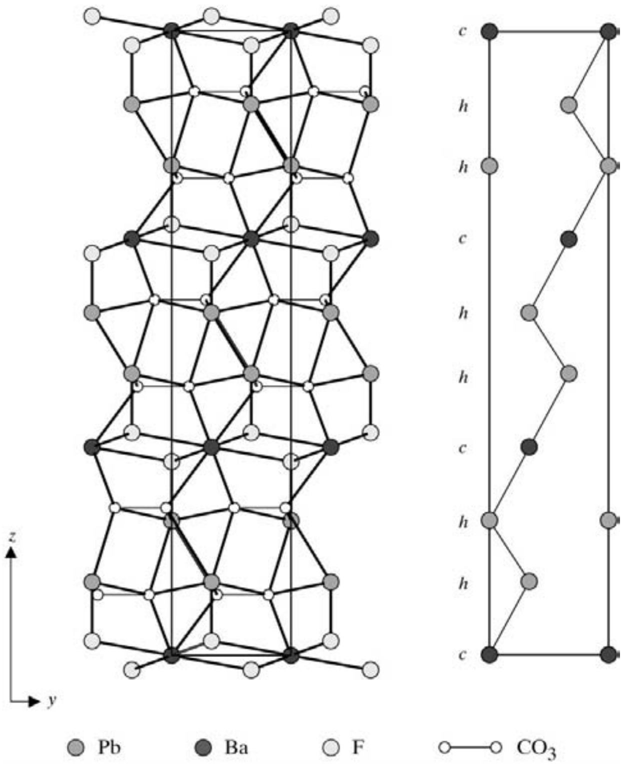

Figure 1
The crystal structure of $(PbCO_3)_2{\cdot}BaF_2$ projected along [100], with the layer-stacking sequence of $[c(h)_2]_3$ along [001].

Recently, the structure of $(PbCO_3)_2{\cdot}Pb(OH)_2$ was solved from single-crystal X-ray data (Pluth & Steele, 2001), as well as from synchrotron X-ray powder data (Martinetto *et al.*, 2002). The main atomic arrangement is similar to that of $(PbCO_3)_2{\cdot}BaF_2$, but in the hydrocerussite structure, one Pb layer is disordered, which corresponds to the Ba layer in the structure of the title compound. The Pb atom is then split

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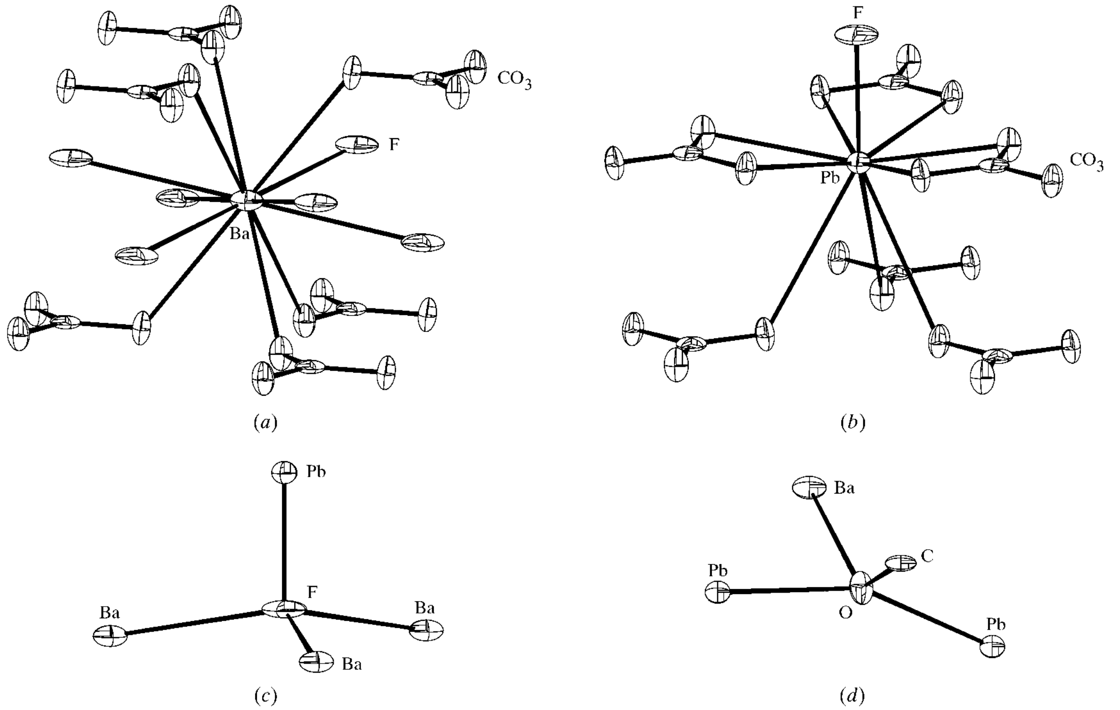

Figure 2
Coordination polyhedra, with anisotropic displacement ellipsoids drawn at the 70% probability level, for (*a*) [BaO_6F_6], (*b*) [$PbFO_9$], (*c*) [FBa_3Pb] and (*d*) [OPb_2BaC].

around the 3*a* site and located on the 18*h* sites with occupancy factors of $\frac{1}{6}$. The different crystal chemical behaviour of $(PbCO_3)_2{\cdot}BaF_2$ and $(PbCO_3)_2{\cdot}Pb(OH)_2$ might be explained by both the lone-pair effect of the Pb^{II} atoms and the hydrogen bonding of the OH groups in comparison with the Ba^{II} and F atoms, respectively.

Additional crystals of composition $(PbCO_3)_2{\cdot}MF_2$ (*M* is Ca, Sr or Pb) have been prepared under similar hydrothermal conditions. They occur as transparent hexagonal plates, with lattice constants of $a = b \simeq 5.20$ Å and a stacking disorder along the *c* axis. Although this reveals a structural analogy between these compounds and $(PbCO_3)_2{\cdot}BaF_2$ or $(PbCO_3)_2{\cdot}Pb(OH)_2$, the corresponding powder diagrams do not indicate a close relationship.

Experimental

According to the formula of the desired product, $Ba_2Pb_4F_{10}Cl_2$, stoichiometric mixtures of KF, KCl, $Ba(Ac)_2$ (Ac is acetate) and $Pb(NO_3)_2$ (all Merck, p.A.) were placed in a Teflon-lined steel autoclave. After filling the reaction chamber with dilute acetic acid (filling degree *ca* 70%) and a reaction time of 20 d at 523 K, colourless single crystals with a hexagonal shape and a maximum diameter of about 0.5 mm had formed. Under these conditions, the acetic acid was oxidized by excess nitric acid [provided by $Pb(NO_3)_2$]. Besides the title compound as the main phase, needle-shaped crystals of $Pb_7F_{12}Cl_2$ (Aurivillius, 1976) were also observed. Single-phase $(PbCO_3)_2{\cdot}BaF_2$ was prepared under similar conditions in demineralized water (523 K for 12 d) from $PbCO_3$ and BaF_2 (Riedel de Haën, pure) in a molar ratio of 2:1 with addition of small portions of NH_4Ac (Merck, p.A.). $PbCO_3$ was obtained by precipitation of a $Pb(NO_3)_2$ solution with excess $(NH_4)_2(CO_3)_2$ (Merck, p.A.). IR spectroscopic measurements did not indicate any incorporation of water or OH^- into the structure of $(PbCO_3)_2{\cdot}BaF_2$.

Crystal data

$(PbCO_3)_2{\cdot}BaF_2$
$M_r = 709.74$
Trigonal, $R\overline{3}m$
$a = 5.1865$ (4) Å
$c = 23.4881$ (8) Å
$V = 547.18$ (6) Å^3
$Z = 3$
$D_x = 6.462$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2163 reflections
$\theta = 2.6$–$29.0°$
$\mu = 51.41$ mm^{-1}
$T = 293$ (2) K
Plate, colourless
$0.22 \times 0.13 \times 0.05$ mm

Data collection

Siemens SMART CCD area-detector diffractometer
ω scans
Absorption correction: numerical (*HABITUS*; Herrendorf, 1993–1997)
$T_{min} = 0.013$, $T_{max} = 0.138$
2535 measured reflections
237 independent reflections
236 reflections with $I > 2\sigma(I)$
$R_{int} = 0.069$
$\theta_{max} = 29.8°$
$h = -7 \rightarrow 7$
$k = -7 \rightarrow 7$
$l = -32 \rightarrow 32$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.020$
$wR(F^2) = 0.044$
$S = 1.34$
237 reflections
19 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0071P)^2 + 10.9202P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 2.38$ e Å^{-3}
$\Delta\rho_{min} = -1.32$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.0061 (3)

Table 1
Selected geometric parameters (Å, °).

Ba—O^{i}	2.850 (5)	Pb—O^{ii}	2.6456 (10)
Ba—F^{ii}	3.0438 (13)	Pb—O^{iii}	3.262 (5)
Pb—F	2.219 (7)	C—O^{iv}	1.290 (5)
O—C—O^{iv}	119.96 (4)		

Symmetry codes: (i) $\frac{1}{3} - x, \frac{2}{3} - y, \frac{2}{3} - z$; (ii) $x - \frac{2}{3}, y - \frac{1}{3}, z - \frac{1}{3}$; (iii) $y - \frac{2}{3}, -\frac{1}{3} - x + y, \frac{2}{3} - z$; (iv) $-y, x - y, z$.

Most of the atoms show a distinct anisotropy of the displacement parameters, with significantly smaller U_{33} values than U_{11} and U_{22} values. This behaviour is attributed to the layer structure of this compound, representing a pronounced interaction within one layer and a weaker interation between adjacent layers stacked along [001]. The crystal shape was optimized by minimizing the internal R value of selected reflections [$I > 20\sigma(I)$] using the program *HABITUS* (Herrendorf, 1993–1997). The habit so derived was used for the numerical absorption correction.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ATOMS for Windows* (Dowty, 1998); software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: IZ1024). Services for accessing these data are described at the back of the journal.

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